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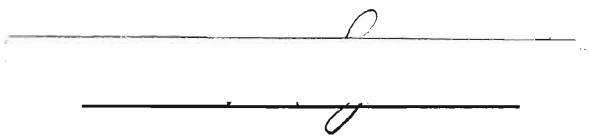

CORROSION OF NICKEL CONTAINING MATERIALS BY CARBON MONOXIDE AT ELEVATED TEMPERATURES

A THESIS

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by

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CORROSION OF NICKEL CONTAINING MATERIALS

BY CARBON MONOXIDE AT ELEVATED TEMPERATURES

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SUMMARY

Corrosive effects of high purity commercial carbon monoxide on AISI Type 304 stainless steel, commercially pure nickel and Inconel were studied at temperatures of 920 to 1100° F. The experimental metal specimens were in the form of small annealed wires which were 0.008 or 0.010 inches in diameter.

All experiments were made at essentially atmospheric pressure. The metal specimens were exposed to carbon monoxide for various times ranging from 4 to 120 hours, although most of the exposure times were 16 hours.

Type 304 stainless steel was found to be the most reactive metal of the three types studied. The reactivity of Type 304 stainless steel with carbon monoxide was about an order of magnitude greater than that of nickel and Inconel for the temperature range studied. Reactivity for the three different types of metals tended to increase with temperature. This trend was particularly noticeable in the case of Type 304 stainless steel at temperatures greater than about 1020° F. The most direct measure of reactivity of the various experimental metal specimens was weight increases due to carbonaceous surface deposits. These surface deposits had a high graphitic carbon content.

Analytical work was done which employed chemical, x-ray diffraction, x-ray fluorescence, electron micro-probe, microscopic and metallurgical techniques. Attempts to define the chemical species involved in the corrosion process resulted in indefinite conclusions.

Most of the experimental work was done on AISI Type 304 stainless steel wires, since Type 304 steel was the most reactive metal studied. Evidence was found that the attack of carbon monoxide on Type 304 stainless steel at temperatures near 1000° F. was, at least in part, intergranular in localized areas. The carbonaceous surface deposits on the stainless steel wires contained measurable amounts of iron and nickel and a small amount of chromium. X-ray fluorescence analysis of the exposed wire surfaces showed that the chromium was retained in the main body of the wires. This supported the analysis of the carbonaceous surface deposits which showed low concentrations of chromium relative to iron and nickel. The carbonaceous deposits were ferro-magnetic even though they contained high concentrations of graphitic carbon which were likely physically attached to the metallic components. X-ray diffraction analysis showed that the experimentally produced carbonaceous surface deposits were very similar to deposits on a specimen of Inconel which had been attacked by gases containing carbon monoxide in industrial service.

Three different corrosion mechanisms were considered possible. These involved formation of an unstable, gas phase, metallic intermediate reaction product, formation of an unstable, solid phase, metallic intermediate reaction product and mechanical wastage of metal by intergranular carbon deposition. Experimental results suggested that formation of an unstable, gas phase, metallic reaction product was the most likely of the three possibilities. Experimental results did not, however, entirely exclude the possibility of formation of unstable, solid phase, metallic reaction products or wastage of metal by mechanical forces due to carbonaceous deposition.

CHAPTER I

INTRODUCTION

Gases containing carbon monoxide destructively affect particular metals of relatively high porosity. This fact has been known for many years. Destructive action of carbon monoxide on such materials as cast iron and similar materials containing iron, nickel, or their oxides was indicated by research done more than a generation ago. The destructive effects were shown to be very pronounced at moderately elevated temperatures, such as near 1000° F. The destruction manifested itself in loss of mechanical strength and ultimate disintegration of the metallic materials. Appreciable quantities of graphitic carbon was formed, in general, in the deleteriously affected areas. Early research workers postulated that the destructive effects of carbon monoxide on cast iron resulted from carbon deposition in the pores of the metal. These depositions were postulated to have generated sufficient mechanical pressures to fracture the metallic material. The carbon formations resulted from carbon monoxide decomposition which was catalyzed by materials such as iron, nickel and their oxides.

Recent industrial experience has shown that dense metals, such as alloy steels and similar materials, have also been deleteriously affected by gases containing carbon monoxide. This destructive action appeared to be similar to that observed on cast iron but, apparently, required longer times for appreciable destruction.

The research work to be presented here was undertaken with the purpose of shedding more light on the mechanism of the destruction discussed above. In particular, the mechanism of destructive effects of carbon monoxide on nickel containing materials was of concern. An experimental program was conducted in which nickel, Inconel, and AISI Type 304 stainless steel wires were exposed to carbon monoxide at temperatures near 1000° F. The results of the experimental work were inconclusive in defining the mechanism of the destructive effects of carbon monoxide on the experimental wire specimens. However, the results indicated that the stainless steel wires, in particular, were deleteriously affected by carbon monoxide. Further, the results suggested that the mechanism of destruction was likely to have involved formation of an unstable, gas phase, metallic intermediate reaction product. However, the possibility of formation of an unstable, solid phase, intermediate product could not be excluded. Also, metal wastage, by mechanical forces due to carbonaceous deposition in metal grain boundary regions, could not be excluded by experimental findings.

Chapter II presents a review of reactions of carbon monoxide with iron, nickel and chromium to form known carbides and carbonyls of the metals. This is given in the interest of presenting some properties of potential unstable intermediate reaction products. Chapter III reviews literature on some related research and industrial experience. Experimental apparatus, procedures and results are presented in Chapter IV. Analysis of experimental results, conclusions and suggestions for further research are given in Chapter V.

CHAPTER II

REACTIONS INVOLVING CARBON MONOXIDE WITH IRON, NICKEL, AND CHROMIUM AT TEMPERATURES NEAR 1000° FAHRENHEIT

Iron and nickel are known to be active catalysts for the decomposition of carbon monoxide to form carbon and carbon dioxide at temperatures in the vicinity of 1000° F. This fact has been known for many years. Experience and research findings have, however, indicated that the chemical processes which take place in systems involving carbon monoxide and these metals are quite complicated. Formation of metallic reaction products and unstable intermediate products, such as metallic carbides, etc., is possible. The following discussion is directed towards presenting information concerning some of the possible reactions of carbon monoxide with iron, nickel and chromium at temperatures near 1000° F.

Generally, one intuitively considers the feasibility of formation of metal carbonyls and carbides when dealing with systems involving carbon monoxide and iron or nickel. The carbonyl possibility arises from direct reaction of the metals with carbon monoxide. For example, the more common carbonyls of iron and nickel are $Fe(CO)_5$ and $Ni(CO)_4$. At moderately low temperatures, circa 100-200° C., these carbonyls can be formed by direct reaction with carbon monoxide and the metals. Chemical equations which describe these reactions are:

$$Fe_{(s)} + 5\ CO_{(g)} = Fe(CO)_{5(g)}$$

$$Ni_{(s)} + 4\ CO_{(g)} = Ni(CO)_{4(g)}$$

These carbonyls are liquid (boiling points- $Fe(CO)_5$: 103° C., $Ni(CO)_4$: 43° C.), but they are gaseous at low pressures, and moderate temperatures. Chromium also forms a carbonyl under very high pressures. Ephriam (1) states that $Cr(CO)_6$ is known to exist but it is not easily formed. Further, he states that of all the metallic carbonyls, only those of iron and nickel can be formed at atmospheric pressure. Pressures of the order of hundreds of atmospheres are required for appreciable formation of $Cr(CO)_6$.

As stated earlier, iron and nickel are known to be active catalysts for the reaction $2\ CO_{(g)} = C_{(s)} + CO_{2(g)}$. The formation of carbon immediately suggests the possibility of carbide formations. Further, experimentation has shown that carbides of iron, nickel and chromium can be formed by reaction with carbon monoxide. However, the carbides of iron and nickel, in particular, are known to be meta-stable and can be readily decomposed at temperatures of 300-400° C.

Thermodynamic Considerations.--For a survey of feasible reactions of carbon monoxide with metals, such as iron, nickel and chromium, one desires, among other things, thermochemical information on reactants (including materials such as alloys) and reaction products. With such information, a general survey of the feasibility of the various possible reactions can be made, under equilibrium conditions. Although equilibrium conditions in some cases may, for all practical purposes, never be attained due to kinetic factors, such an analysis is generally quite desirable in the formative stages of research work. Quite often, literature on thermodynamic properties of the various chemical species is lacking,

even for pure materials. Lack of information is commonly the case, in particular, for materials such as alloys. In the course of the work undertaken here, the following tables of free energies of formation of the more common carbides of iron, nickel and chromium were obtained from technical literature. Also included here are standard free energies of formation of $Ni(CO)_4$ and free energies of reaction for the decomposition of carbon monoxide. No free energy data were located in the case of $Fe(CO)_5$.

Table I

Standard Free Energies, ΔF°, as Functions of Temperature, °K.

Reaction	ΔF°, calories	Reference
$23/6\ Cr + C = 1/6\ Cr_{23}C_6$	$-16,380 - 1.54T^*$	(2)
$7/27\ Cr_{23}C_6 + C = 23/27\ Cr_7C_3$	$-10,050 - 2.85T^*$	(2)
$3/5\ Cr_7C_3 + C = 7/5\ Cr_3C_2$	$-3,200 - 0.20T^*$	(2)
$3\ Fe + C = Fe_3C$	$+6,200 - 5.53T^{**}$	(2)
$3\ Fe + C = Fe_3C$	$+6,380 - 5.92T^{***}$	(2)
$3\ Ni + C = Ni_3C$	$+8,110 - 1.70T^{****}$	(2)
$Ni + 4\ CO_{(g)} = Ni(CO)_4$	$-31,972 + 87.92T$	(3)
$2\ CO_{(g)} = CO_{2(g)} + C$	$-40,800 + 41.7T$	(2)

Except where indicated to be ideal gases, (g), standard states are solids.

*Temperature range: 298 - 1673°K., variability - 3 K-cal.

**Temperature range: 298 - 463°K., variability - 1 K-cal.

***Temperature range: 463 - 1115°K., variability - 1 K-cal.

****Temperature range: 298 - 1000°K., variability - 3 K-cal.

In addition to the above thermodynamic data, tabulated standard free energies of formation of carbon monoxide and carbon dioxide were obtained from publications of the United States Bureau of Standards (4). This information is reproduced in the following table.

Table II

Standard Free Energies of Formation, ΔF°, of Carbon Monoxide and Carbon Dioxide as Functions of Temperature

Temperature (°K)	ΔF°: $C + 1/2\ O_2 = CO$ (K-cal.)	ΔF°: $C + O_2 = CO_2$ (K-cal.)
298.16	-32.8079	-94.2598
300	-32.8464	-94.2603
400	-35.007	-94.325
500	-37.184	-94.392
600	-39.358	-94.444
700	-41.526	-94.497
800	-43.677	-94.539
900	-45.816	-94.578
1000	-47.942	-94.610

Standard states: C - graphite; O_2, CO, CO_2- ideal gases.

Figures 1 and 1a were prepared by using the thermodynamic functions of Table I. Figures 1 and 1a are graphs of the equilibrium constant, K_a, on logarithmic scale, versus temperature for various reactions. Because of large numerical magnitude differences in equilibrium constants, Figure 1 was prepared in two parts. Figure 1 is concerned with reactions of iron

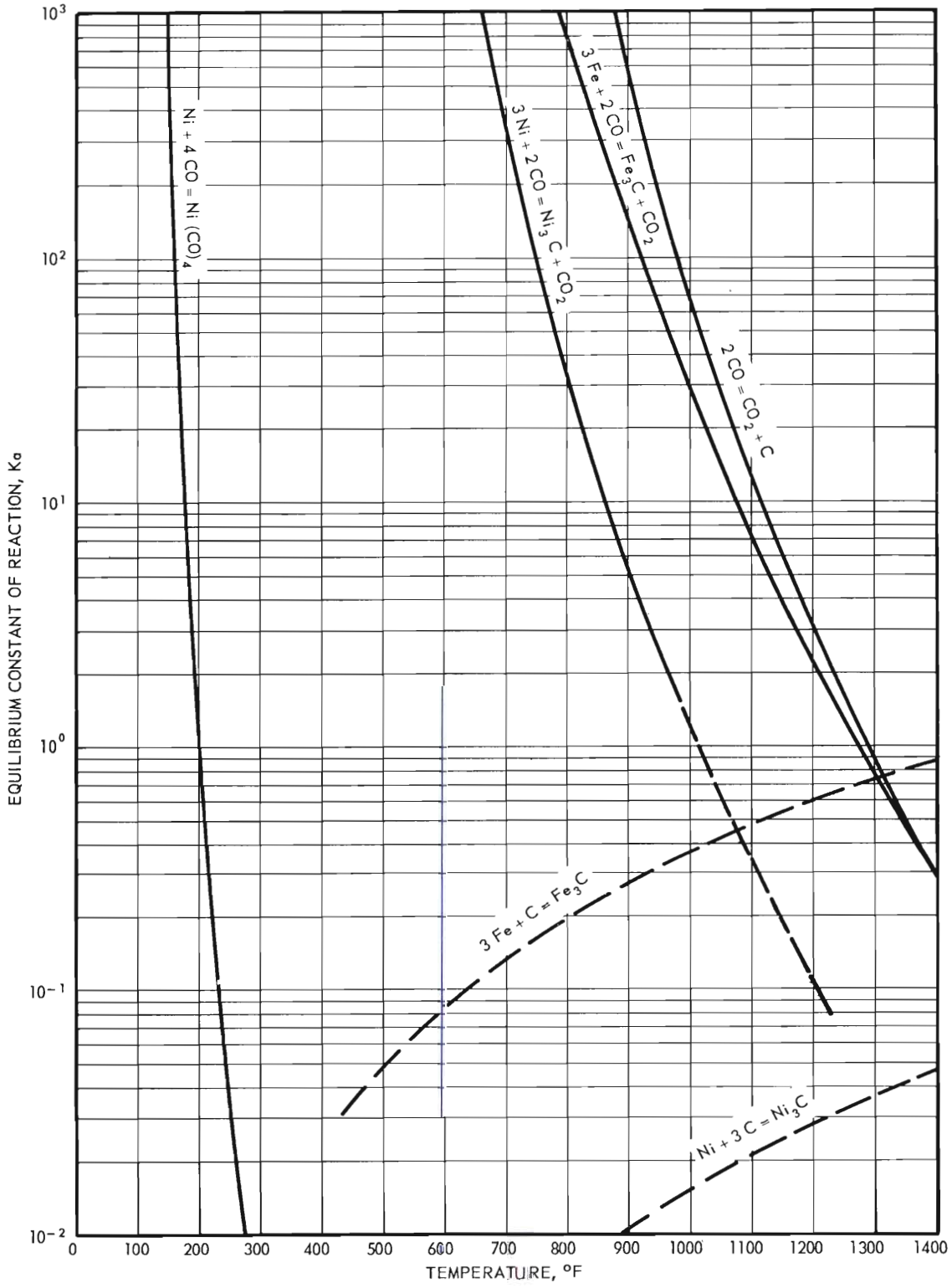

Figure 1. Equilibrium Constants Versus Temperature.

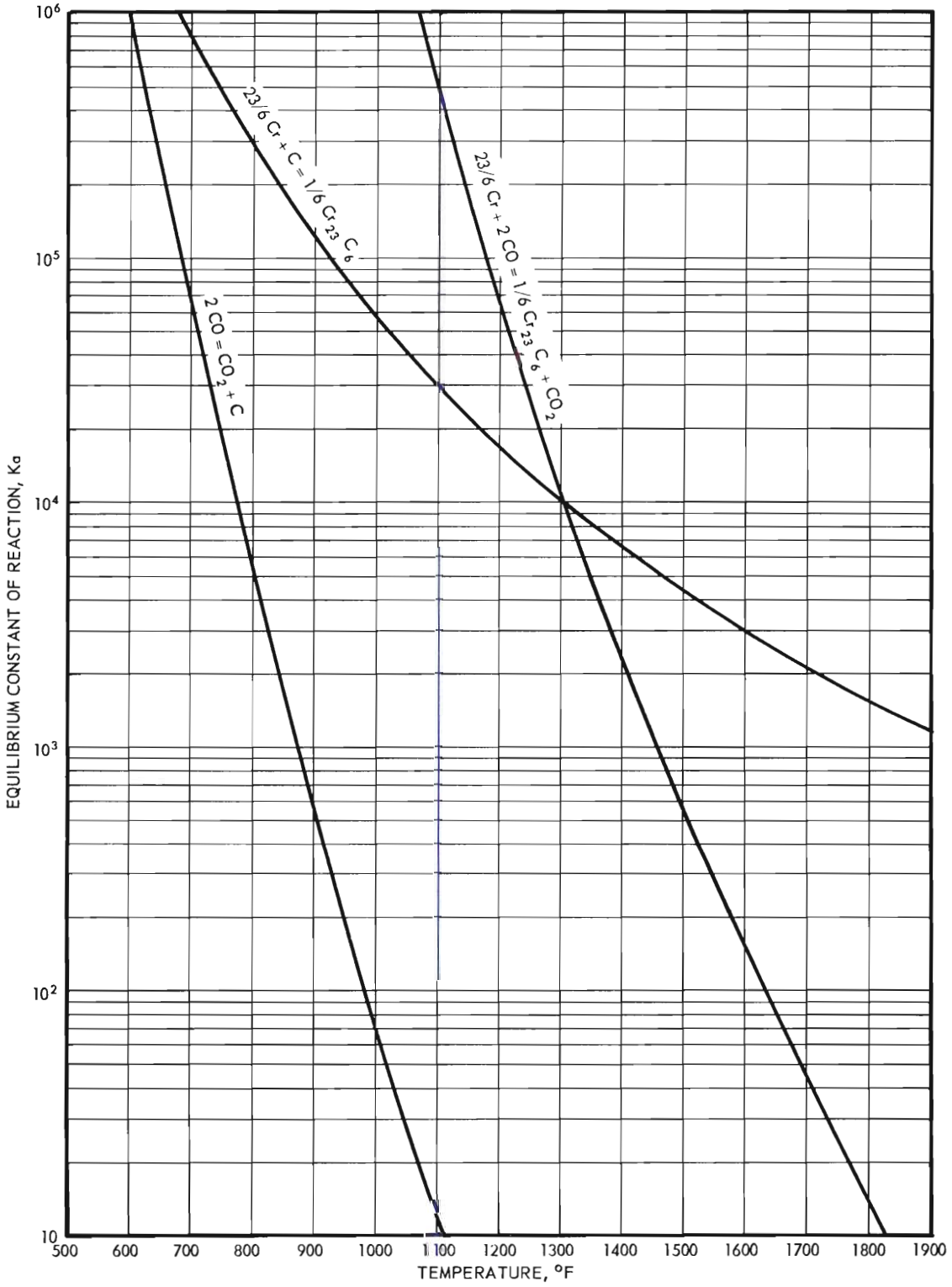

Figure 1a. Equilibrium Constants Versus Temperature.

and nickel and Figure 1a deals with reactions involving chromium. Included here are those reactions in which nickel carbonyl and the carbides of iron, nickel and chromium are formed from reaction of carbon monoxide, or carbon, with the metals. Also shown in these graphs are the equilibrium constants for the decomposition of carbon monoxide to form carbon and carbon dioxide. The carbon monoxide decomposition calculations based on the equation of Table I are in good agreement with those based on the tabular data of Table II. This is illustrated in the following comparison.

Standard Free Energies, ΔF°, for the Reaction: $2CO = CO_2 + C$

Temperature, °K	300	500	700	900
ΔF° (Table II), K-cal.	-28.5675	-20.024	-11.445	-2.946
ΔF° (Table I), K-cal.	-28.290	-19,950	-11.610	-3.270

Clearly, Figure 1 illustrates that the most common nickel carbonyl and carbides of both iron and nickel are thermodynamically unstable at temperatures near 1000° F. In the case of nickel carbonyl, thermodynamic instability is supported by the fact that the equilibrium constant, K_a, is calculated to be about 10^{-21} at 1000° F. The arguments are somewhat different in the case of the carbides since three solid phases are involved when the carbides decompose. However, the conclusion is clearly the same, i.e., thermodynamic instability. Since standard free energies for these reactions are negative (for decomposition), one would expect complete decomposition of these carbides, near 1000° F., at equilibrium. On the other hand, Figure 1a indicates that the carbides of chromium are thermodynamically stable near 1000° F.

Figure 2 gives equilibrium CO/CO_2 molal ratios and CO concentrations as functions of temperature. The temperature range of this graph is 800 to 1300° F. These molal ratios and compositions apply to pure $CO\text{-}CO_2$ mixtures, in contact with solid carbon, at one atmosphere absolute pressure. Calculations for this graph were based on standard free-energy information given in Table II. Pure carbon monoxide is thermodynamically unstable over the entire temperature range of Figure 2.

General Review of Literature on Carbides and Carbonyls.--

The carbides and carbonyls discussed above are not, by any means, the only carbides and carbonyls of iron, nickel and chromium. For example, Ephriam (1) lists the following carbonyls to have been chemically identified - $Fe(CO)_5$, $Fe_2(CO)_9$, $\left[Fe(CO)_4\right]_3$, $Ni(CO)_4$ and $Cr(CO)_6$. Schwarzkopf et al (5) state that there are three carbides of chromium which are certain to exist. They are $Cr_{23}C_6$ (old Cr_4C), Cr_7C_3 and Cr_3C_2. These authors further state that a carbide, CrC, apparently exists at temperatures greater than 2000° C., but this decomposes upon cooling into Cr_3C_2 and carbon. Ni_3C appears to be the only well established carbide of nickel, although Bernier (6) indicates the possible existence of Ni_4C and Hofer, Cohn and Peebles (10) state that Ni_6C has been identified. In addition to the well known cementite structure, Fe_3C, a number of authors have indicated the existence of $Fe_{20}C_9$ (old Fe_2C). Further, "iron graphite" is frequently mentioned in technical literature.

Hofer (7) gives a rather extensive discussion of the properties of metal carbides, including those of iron, nickel and chromium. Hofer states that nickel carbide, Ni_3C, decomposes above 420° C. Although the carbides

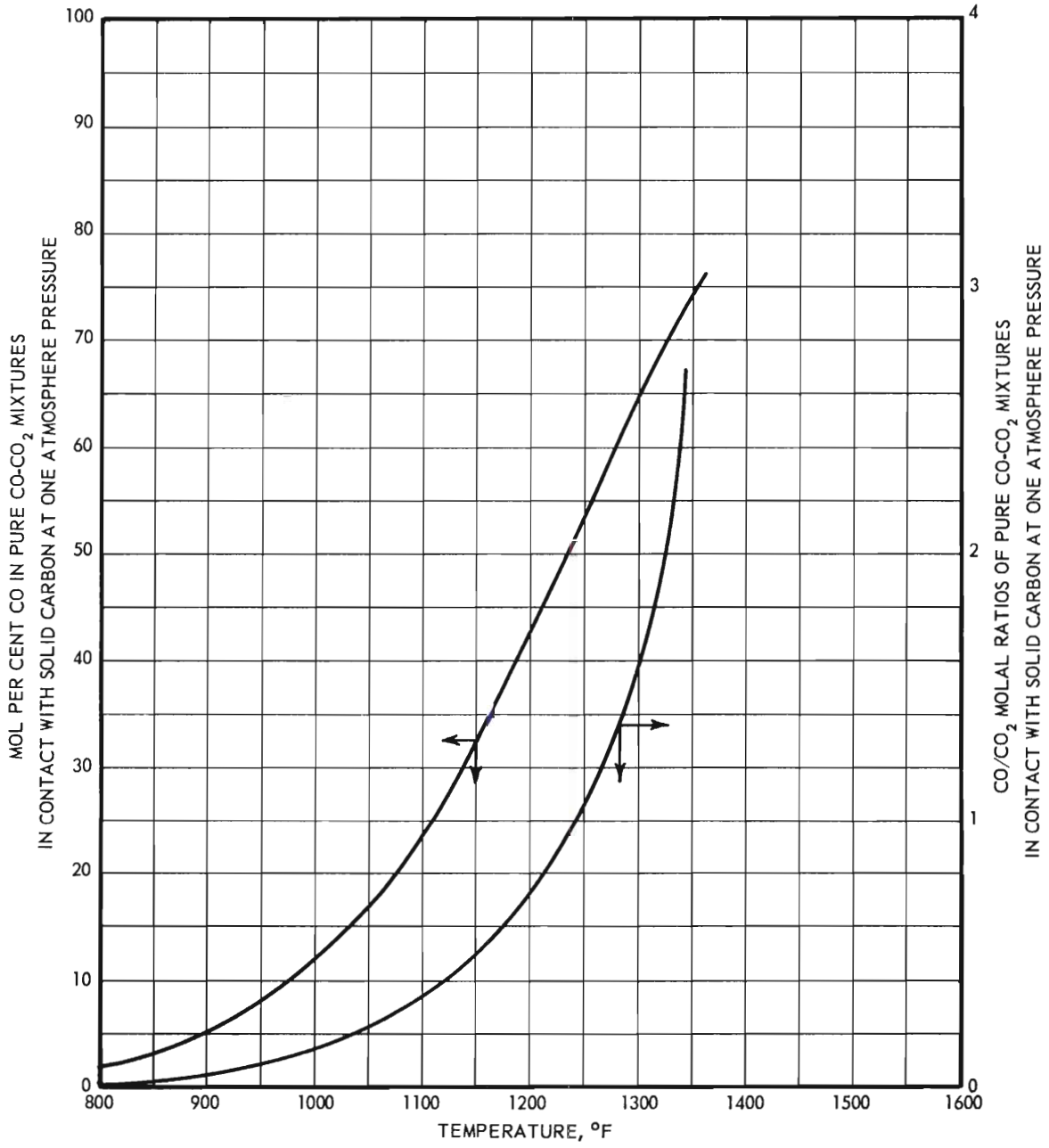

Figure 2. Equilibrium Concentrations of CO in Pure CO-CO_2 Mixtures, at One Atmosphere Pressure Versus Temperature.

of iron can be formed by reaction of iron with carbon monoxide at temperatures of about 250° C., Hofer suggests that these carbides are only metastable. Further, he infers that it is doubtful that iron carbides are stable at any temperature. Hofer, Cohn and Peebles (8) state that the existence of two carbides of iron of the Fe_2C type was confirmed (Pichler and Merkel, Ph.D. thesis, Kaiser Wilhelm Institute, Kohlenforsch). These carbides are reported to have Curie points of 247° and 380° C. Jack (9) reports some interesting data on the stability of $Fe_{20}C_9$. These data are the result of heat treating $Fe_{20}C_9$ and Fe_3C for various times at controlled temperatures. Resulting products, after heat treatment, were determined. His results are reproduced as follows.

Starting Material	Temperature (°C)	Time	Products
$Fe_{20}C_9$	350	50 hours	$Fe_{20}C_9$
$Fe_{20}C_9$	450	30 hours	Fe_3C, carbon, α-iron
Fe_3C	450	8 days	α-iron, carbon, Fe_3C
Fe_3C	550	4 days	α-iron, carbon, trace Fe_3C
Fe_3C	1000	7 minutes	α-iron, carbon, trace Fe_3C

Bernier (6) is reported to have studied the thermal stability of carbides of iron, nickel and mixtures of iron and nickel in different gaseous atmospheres. An abstract on this work is quoted, in part, as follows:

> Passing a mixture of CO + $2H_2$ at 170°, or pure CO at 300° over Ni reduced and dispersed on ThO_2 causes insertion of C atoms in the hexagonal Ni lattice to form a series of paramagnetic hexagonal carbides with the limiting formula Ni_3C. At 210° this changes to a ferromagnetic, face centered cubic carbide with limiting formula Ni_4C. The hexagonal form loses C to give pure Ni at 276° in N, 450° in CO, and 171° in H ... Pure cementite results from passing

CO + 2 H_2 over Fe dispersed on Fe_2O_3 at 560° and 1000°. Direct synthesis from the elements occurs at 800° in vacuum. The formula approaches Fe_3C. Loss of C occurs at 590° in H and 640° in N. No other carbide is formed. Treatment of Fe-Ni alloys with CO + 2 H_2 at 170-560° results in carbide formation. The stability of the product increases with increasing Fe content, but does not reach the stability of pure cementite. With alloys containing 0-40% Ni, only an orthorhombic, ferromagnetic carbide is formed, resulting from replacement of Fe by Ni in the cementite lattice. With 70-100% Ni alloys, the hexagonal Ni carbide exists, with replacement of Ni by Fe atoms. Between 40 and 70% Ni, the two phases coexist.

Hofer, Cohn, and Peebles (10) made an extensive kinetic study of the decomposition of Ni_3C. The decompositions were carried out at 325 and 355° C. A secondary interest in this work was to investigate possible lower carbide formations such as Ni_6C. They concluded that no lower carbides formed. They found that an induction period preceded the decomposition process for Ni_3C. For example, at 355° C., about 100 minutes lapsed before Ni_3C began to decompose significantly. From about 70 to 10 per cent nickel carbide, the decomposition was approximately zero order. Using the zero order rate constant which was experimentally determined, a half life (after induction) for Ni_3C at 355° C., was calculated to be 0.26 hours.

The carbonyls of both nickel and iron are known to be thermally unstable even at moderate temperatures. For example, Ephriam (1) states that $Fe_2(CO)_9$ decomposes at 100° C. and $\left[Fe(CO)_4\right]_3$ readily decomposes at 140° C. For many years, pure nickel has been made industrially by a refining process (Mond Process) which involves thermal decomposition of $Ni(CO)_4$. The carbonyl of nickel is formed (gas phase) in this process at about 80° C. This gas stream is diverted to a decomposition chamber where the carbonyl is decomposed on nickel shot at about 300° C (11).

Mond and Wallis (12) showed that $Fe(CO)_5$ could be prepared most readily at temperatures very near 200° C., employing various pressures up to 300 atmospheres. At every pressure, the optimum temperature was very near 200° C. The yield of $Fe(CO)_5$ decreased to nearly zero at temperatures above 300° C. and less than about 100° C., even at 300 atmospheres pressure.

In summary, all the carbides and carbonyls of nickel and iron, with known properties, are thermodynamically unstable near 1000° F.

CHAPTER III

OTHER RELATED RESEARCH WORKS AND INDUSTRIAL EXPERIENCE

Although investigations of the reactions of carbon monoxide with metals containing iron, nickel, cobalt and other similar substances have been made in the past, examination of these findings indicates that further research is well justified. In particular, the mechanism (or mechanisms) of the destructive effects of carbon monoxide on engineering materials at moderately elevated temperatures has never been satisfactorily described. Strong evidence, from both prior research work and industrial experience, has already been given which indicates that carbon monoxide containing gases attack some of the common engineering alloys "corrosively" at temperatures in the vicinity of 1000° F. The temperature range at which these effects are appreciable is not very well defined but appears to be from about 900 to 1400° F. The temperatures of most severe attack depend upon the particular metal substances involved. Brief reviews of some of the more pertinent literature concerning the destructive effects of gases containing carbon monoxide and possible mechanisms of the destruction are given in the following pages. One readily gathers from this information that:

1. Iron, nickel and cobalt are catalytically active for the decomposition of carbon monoxide to carbon dioxide and carbon, at suitable temperatures.
2. The common metal substances, which catalyze the decomposition of carbon monoxide are typically carbide formers, although the reverse is not true.

3. Decomposition of carbon monoxide to carbon dioxide and carbon appears to be favored, in the presence of suitable catalysts, at temperatures of the order of 850 to 1500° F.
4. Mechanisms for the destructive effects of carbon monoxide on materials such as cast iron, steels and alloy steels may involve the formation of carbides (stable or unstable), deposition or diffusion of graphitic carbon in the pores, or grain boundaries, of the metals, or formation of unstable intermediates such as carbides or carbonyls.
5. Addition of such substances as silicon, molybdenum and chromium to alloy steels may enhance the resistance of the steels to attack by carbon monoxide. It appears, however, that in the case of chromium rather large additions (of the order of 25 per cent) are necessary.
6. Addition of small amounts of sulfur containing materials, or ammonia, to the carbon monoxide containing gases may reduce the destructive effects of the gases on the engineering materials.

Other Related Research Works :

Work of Baukloh and Hieber (13) and Baukloh (14, 15).--Baukloh and Hieber conducted a research program in which Fe, Fe_2O_3, Fe_3O_4, Co_3O_4, Co, Ni, NiO, Ni_2O_3, Cr, Cr_2O_3, Mn, MnO_4, Al, Zn, ZnO and CuO were subjected to carbon monoxide at temperatures ranging from 450 to 850° C. This work was done in the interest of explaining the mechanism of disintegration

of iron ore in the presence of carbon monoxide. Disintegration of iron ores had been observed many times when the ores were reduced by carbon monoxide. Baukloh and Hieber concluded that the disintegration of iron ore was brought about by the formation of carbon in the pores of the ore lumps. They postulated that the carbon formed at catalytically active sites in these pores and continued to form there until mechanical pressures from the decomposition literally fractured the ore lump. The carbon formation was due to decomposition of carbon monoxide according to the reaction $2\ CO = CO_2 + C$.

The above reaction, as had already been established, requires suitable catalysts even at thermodynamically favorable conditions. Equilibrium $CO\text{-}CO_2$ compositions as functions of temperature at one atmosphere pressure, for pure $CO\text{-}CO_2$ gas mixtures in the presence of solid carbon, is given in Figure 2, page 11.

The research conducted in these investigations indicated that iron, nickel, cobalt and their oxides were relatively active catalysts for the decomposition reaction above. To establish catalytic activity as a function of temperature, powdered samples of the various metals and oxides were exposed to pure carbon monoxide at controlled temperatures for thirty minutes and/or three hours. The powders were screened through sieves with 4900 meshes per square centimeter, and only the material passing through the sieves was used. Erratic temperature versus carbon deposition rates were presented in graphical form by Baukloh and Hieber, except in the case of iron and its oxides. For iron and its oxides, carbon deposition rates were indicated to steadily increase with temperature

from about 350° C. to a maximum at about 550° C. From the 550° maximum, a steady decrease to a non-appreciable deposition rate at about 750° C. was indicated at the higher temperatures. As stated earlier, the temperature-carbon deposition rate curves were rather erratic for the materials other than iron and its oxides. For this reason, it is difficult to conclude where maximum deposition rates actually occur. Further, it is difficult to rank the various materials as to their relative catalytic activity. However, the ranking, in Table III, shows approximate relative activities, with the most active materials appearing at the top of the table with activity decreasing downward. This table was prepared from data given in Figures 4-7 of Baukloh and Hieber (13).

Table III

Approximate Relative Catalytic Activity of Various Materials for the Decomposition of Carbon Monoxide

Material	Temperature of Maximum Carbon Deposition, °C.	Approximate Maximum Deposition in ½ Hour, grams
Fe_2O_3	550	0.75
Fe_3O_4	550	0.74
Fe	550	0.40
NiO	450	0.30
CoO_4	650	0.25
Co	650	0.15
Ni	750	0.15
Ni_2O_3	450	0.09
Mn	850	0.02
Cr	650*	0.005
Al	550	0.002
Al_2O_3		no appreciable deposition
Cr_2O_3		no appreciable deposition
Cu		no appreciable deposition

(continued)

Table III (continued)

Approximate Relative Catalytic Activity of Various Materials for the Decomposition of Carbon Monoxide

Material	Temperature of Maximum Carbon Deposition, °C.	Approximate Maximum Deposition in ½ Hour, grams
CuO		no appreciable deposition
Mn_3O_4		no appreciable deposition
Zn		no deposition below volatilization temperatures.
ZnO		no deposition below volatilization temperatures.

*Not tested at any higher temperatures because of melting point.

Baukloh and Hieber also concluded that the oxides thermselves were not catalytically active for the decomposition reaction. However, the nascent metals, from the reduction of the oxides by the carbon monoxide, were the active catalysts and, in general, were more active than the metals themselves.

Later, Baukloh (14) presented an article in which he proposed to explain the mechanism of destruction of cast iron by carbon monoxide containing gases. A piece of cast iron which had been exposed to carbon monoxide containing gases for about eighteen months at 500-600° C. had been found to be partially disintegrated into a powder or dust. This powder contained about thirty per cent carbon. Further inspection of the piece of cast iron disclosed large deposits of carbon in pores and grain boundaries. Baukloh felt that this destruction of the cast iron was caused by decomposition of carbon monoxide into carbon dioxide and carbon. Further, he felt that the destruction was of the same nature

as that for iron ore which he and Hieber (13) had studied earlier. That is, the destruction was brought about by the deposition of carbon in the pores of the metal as the metal catalytically decomposed the carbon monoxide.

In a second article, Baukloh (15) discussed further research findings which were associated with the destructive effects of gases containing carbon monoxide on metals and their oxides. Compressed cubes of CaO, CuO, Cr_2O_3, CaO plus one per cent Fe_2O_3, Fe_2O_3 and Ni_2O_3 were subjected to carbon monoxide for one hour at 550° C. In the case of Fe_2O_3 and Ni_2O_3, the compressed cubes were affected so strongly that they disintegrated easily with a very small impact. The CaO and Cr_2O_3 cubes showed no decomposition phenomena, nor was any carbon deposited. The CuO cube expanded slightly due to reduction of the oxide to copper. The CaO cube, containing one per cent Fe_2O_3, was completely destroyed. Baukloh related this to his earlier works in connection with the destruction of iron ore and cast iron by carbon monoxide. Further, he pointed out that the attack of carbon monoxide appeared to take place with those metals that were typical carbide formers. This opinion was based on the prior work of Baukloh and Hieber (13) and on the fact that the CuO, was unaffected. He stated that dense metals, such as steels, even though likely catalysts for the decomposition of carbon monoxide, are not attacked by carbon monoxide destructively. This, he felt, was because the carbon monoxide cannot diffuse into the steels but can only migrate in them in atomic from.

Work of Leidheiser and Gwathmey (16) and Kehrer and Leidheiser (17).--In 1948, Leidheiser and Gwathmey published a technical paper dealing with, among other things, the relative catalytic activity of the different crystal faces of nickel single crystals for the decomposition of carbon monoxide. This work indicated that the (111) faces (or the {111} pole area) were the most active catalytic crystalline planes for the decomposition of carbon monoxide to carbon dioxide and carbon. Decomposition reactions were carried out at 550° C. in a static system using approximately one liter of pure carbon monoxide, initially, and single crystals. These single crystals were 3/8 to 5/8 inch in diameter, with about 5 square centimeters surface area. In these studies, it was found that the carbon could be dusted from the surface of the crystals rather easily at first, but later, the carbon became more tenacious. The major product on the metal surface was carbon, although the presence of an intermediate carbide was not excluded. In some tests employing nickel foil, analysis of the surface product gave 88.52 weight per cent carbon and 11.01 weight per cent nickel. Results similar to those using pure carbon monoxide were obtained at 550° C. with hydrogen and carbon monoxide mixtures, when carbon monoxide was in excess. When the carbon monoxide concentration was as low as 10 per cent, no carbon was deposited.

Later, Kehrer and Leidheiser (17) reported on the decomposition of carbon monoxide catalyzed by single crystals of nickel. They too found that regions surrounding the (111) faces of the crystals were the most active catalytically. Carbon depositions, similar to those above, were formed in microscopic pits of approximately hemispherical shape, when

carbon monoxide decomposed on flat single crystals. X-ray diffraction analysis of the products of reaction on the (111) faces indicated only the presence of graphitic carbon. However, as stated above, chemical analysis had indicated the presence of nickel in the carbon deposits as reported by Leidheiser and Gwathmey.

Work of Hofer, Sterling, and McCartney (18).--Hofer, Sterling and McCartney reported on the structure of carbon deposited by carbon monoxide decomposition in studies using electron microscopy. From electron microscope studies and X-ray diffraction analysis, it was concluded that carbon deposited by carbon monoxide decomposition on the metals exhibits filament like physical structures. These thread-like structures appeared to contain denser nuclei which may have been metal carbides and/or metal oxides, from which the filaments grew. Although the structures were similar for the three metals, there were minor differences in them. Thus, whereas the deposits on iron appeared to be solid single filaments, the carbon deposits on cobalt appeared sometimes to be single filaments and other times to be bifilaments or tubules. The deposits of carbon on nickel appeared to be bifilaments almost always. Positive identification of the metallic nuclei was not possible with X-ray diffraction. However, this report stated that the following compositions were suggested by the analyses.

Metallic Surface	Nuclei Composition
Iron	Hagg iron carbide and alpha iron.
Cobalt	Cubic beta cobalt.
Nickel	Indefinite.

It should be pointed out here, with emphasis, that the above carbon monoxide decomposition reactions were carried out at about 390° C. Most other literature discussed in the following pages is concerned with temperatures of about 500° C. and greater.

Work of Skinner and Raudebaugh (19).--Skinner and Raudebaugh, of International Nickel Company, Inc., have conducted some preliminary experimental work in which a number of metallic materials were exposed to carbon monoxide, at one atmosphere pressure, within the temperature range of 1000 to 1200° F. The materials exposed to carbon monoxide included small annealed strips of Inconel, Incoloy, AISI Types 304 and 430 stainless steel, and small specimens of gray iron and ductile iron.

In the first experiments, the annealed strips of Inconel, Incoloy and Types 304 and 430 stainless steel were exposed to the carbon monoxide. These experiments failed to produce any carbonaceous deposits in the reaction zone or any observable attack of the metal specimens with exposure times of 70 hours. Next, gray iron and ductile iron specimens were exposed to the cylinder carbon monoxide for 125 hours at about 1050° F. With both the gray iron and ductile iron specimens, a loose sooty deposit was formed, in appreciable amounts, on the specimens and in the reaction zone. Also, appreciable deterioration of the metal specimens had taken place, as indicated by further analysis. Following the tests on the cast irons, specimens of Type 304 stainless steel, Incoloy and Inconel were simultaneously exposed with gray iron at 1050° F. for 125 hours in attempts to induce reaction in the previously unaffected materials. These tests resulted in localized deterioration of Type 304 stainless steel.

Analysis of the various exposed specimens revealed the following facts:

1. The gray iron experienced more deterioration than the ductile iron.
2. The sooty deposit on the cast iron specimens was ferromagnetic, although no metal particles were visually discernable.
3. Chemical analysis of a sample of the sooty deposit, indicated 65 weight per cent carbon, 26 weight per cent iron, and 0.5 weight per cent nickel. This deposit was formed when cast iron and ductile iron had been exposed to carbon monoxide for 125 hours at 1050° F.
4. Microscopic examination of the various specimens indicated a fair degree of carbon penetration into the cast iron specimens in general, and localized penetration into the Type 304 stainless steel (when reaction was induced by cast iron).
5. Also, the microscopic examination showed, in the case of cast iron specimens, quite a few detached pieces of the metal in the adherent surface carbonaceous deposits.
6. In the case of Type 304 stainless steel, localized deterioration resulted in detachment of metal grains imbedded in the surface carbonaceous deposits also.
7. One sample of Type 304 stainless steel was subjected to mild intergranular corrosion prior to exposure to the carbon monoxide. In this case, graphite penetration was indicated to be of much higher degree than with the other Type 304 specimens.

Experience of Phillips Petroleum Company (20).--Phillips Petroleum Company has experienced not only corrosion problems with various engineering materials but also has experienced fouling of process equipment due, apparently, to corrosion of the process equipment. These problems were encountered in a process where butane was catalytically dehydrogenated for the production of butenes. In this system, a fixed bed of chromia-alumina catalyst was contacted with a butane rich gaseous stream at about 1100° F. Periodically, the catalyst in the reactors were regenerated by burning off carbon. This carbon was formed during the reaction step due to minor amounts of hydrocarbons being cracked. The method used for limiting temperatures below about 1300° F, during the regeneration step, was restriction of the air rate. Thus, the regeneration, or burning operation, took place with an oxygen lean gas and, hence, potentially led to relatively high carbon monoxide content product gas. In connection with this process, various materials of construction (usually iron based nickel and/or chromium alloys) were tested in attempts to find suitable materials of construction. Corrosive effects were observed in these tests. However, of equal importance, if not of more importance, were the fouling effects involved in this system. It was felt that small amounts of the materials of construction, during the corrosion process, were removed and redeposited in the catalyst bed. These materials were catalytically active for undesirable reactions with the hydrocarbon feed gas. These undesirable reactions led to increased carbon deposition. This carbon deposition was the apparent cause of fouling.

To circumvent the above mentioned problems, Phillips Petroleum Company tested various materials of construction in laboratory experiments,

in attempts to determine satisfactory construction materials. The laboratory equipment and operating conditions simulated the plant reaction system. From these tests, various construction materials were rated as follows:

Alloys with Good Ratings	Materials with Poor Ratings
31 Cr - 9 Ni	20 Cr - 3 Ni
27 Cr	18 Cr - 11 Ni
24 Cr - 15 Ni	17 Cr - 13 Ni - 2 Mo
20 Cr - 10 Ni - 3.6 Mo	12 Cr
18 Cr - 12 Ni - 2.5 Si	9 Cr - 1.4 Mo
30 Cr - 65 Co - 4 W	Duriron
	Iron
	Nickel

In the above, where the analyses (weight per centages) are not complete, the balances are iron, except for small amounts of impurities. It should be pointed out that the above ratings were made on the basis of fouling due to carbon formation and that corrosive effects are inferred by such ratings.

The following stainless steels were tested by Phillips Petroleum Company on plant scale equipment.

AISI Type 302 B	AISI Type 304	AISI Type 310
AISI Type 316	AISI Type 321	AISI Type 347

Of these, only Types 302 B, 310 and 316 gave satisfactory operations without plugging of the reactors due to fouling. Type 316 appeared to yield the greatest carbon formation of these three materials.

Analysis of some carbonaceous deposits from one system containing iron revealed only the presence of carbon and Fe_3O_4. After burning this sample, the residual material indicated only Fe_2O_3. Analysis of a carbonaceous deposit from an Inconel reactor indicated only graphite and NiO. These analyses were made using X-ray diffraction techniques.

Experience of Babcock and Wilcox Company (21).--Rather severe corrosion of materials of construction were observed by the Babcock and Wilcox Company in a waste heat boiler. This boiler was operated at about 700-2500° F. and 315 p.s.i.g. Severe attack was experienced with AISI Types 310 and 347 stainless steels. Temperature ranges, where attack was observed, were from about 800 to 1650° F. The corrosive atmosphere was synthesis gas (principally carbon monoxide and hydrogen) produced by burning methane with oxygen under controlled conditions. Periodic steam atmospheres also may have added to the corrosion problem. Above about 1000° F., localized carburization - decarburization was indicated at the affected areas. In these zones, the corrosion was of a pitting nature. At lower temperatures, of the order of 900 to 1000° F., little carburization was observed and the corrosion was rather uniform instead of localized.

After the above corrosion experience, the Babcock and Wilcox Company conducted experiments in which test specimens of various metals were placed in the waste heat boiler. The specimens were placed on baffles in the boiler where the temperatures were approximately 700, 900, 1100, 1300, 1500 and 1700° F. In the first test, exposure time, under operating conditions, was 14 days. In another test, exposure

time was 33 days. For these tests, the samples were weighed before and after exposure and the results were recorded as percentage weight changes. Some of these test results are given in Table IV. Table IV was reproduced from a paper presented at the 1959 Annual Conference of the National Association of Corrosion Engineers.

Table IV*

Weight Changes of Material Samples Installed in the Generator During Second (14 Days) Operating Period

	Material	% Weight Change at Baffle					
		3	5	7	9	11	13
1	Croloy 1½	7	23.2	59.2	58.3	53.7	8.2
2	Croloy 2¼	9.3	22.1	45.1	20.2	44	6
3	Croloy 5	8.9	30.6	51.7	25.9	36.7	5.6
4	Croloy 7	5.2	28.3	50.3	26.3	35.2	5.2
5	Croloy 9	5.5	23	58	24	34.5	5.3
6	Croloy 12 (Type 410)	4.1	31.6	59.1	28	38.4	2.5
7	Croloy 27 (Type 446)	1.8	0.8	2.2	2	2.3	0.9
8	Croloy 18 (Type 430)	3	29.2	45	33.6	22.9	0.7
9	18-8 Type 304	7.7	16.8	37.9	27.5	18.5	0.5
10	18-8 Type 304L	5.7	16.2	41.2	23.3	17.6	0.5
11	16-13-3 Type 316	4.7	19.1	28.8	15.4	12.4	0.1
12	16-13-3 Type 316L	2.9	21.3	22	15.8	14.7	+0.5
13	18-8Cb Type 347	2.9	6.2	23.4	16.4	27.5	+0.2
14	25-20 Type 310	2.2	2.4	19.1	13.5	58.9	+0.1
15	Armco 17-14CuMo	2.4	24.2	63.4	48	11.6	+0.8
	18-8 (Type 304), Aluminized	+2.8	+2.3	8.5	--	1.3	6.9
	25-20 (Type 310), Aluminized	2.2	2.2	7	--	1	2.7
	Inconel, Aluminized	+1.2	+4.1	2	--	2.8	6.9
	25-20 Ceramic Coated	3.7	8.6	58.6	--	2.9	2.2
	18-8 Ceramic Coated	2.5	55	--	94.2	--	2.2
	Carbon-Steel Ceramic Coated	2.6	--	82.1	--	--	18.2
	Carbon Steel	--	--	39.5	--	--	--
	CMo Steel	--	--	40.2	--	--	--
	Copper	--	--	4.4-9.2	--	0.3	1.8-2.6
	Aluminum Bronze	--	--	--	--	--	2.8

*Reproduced from Table I of Paper Number 15 presented at the Fifteenth Annual Conference of the National Association of Corrosion Engineers, Chicago, Illinois, March 16-20, 1959.

The various baffles, indicated in Table IV, were in locations in which approximate temperatures were as follows:

Baffle Number	Approximate Temperature.
3	1700 degrees F.
5	1500 degrees F.
7	1300 degrees F.
9	1100 degrees F.
11	900 degrees F.
13	700 degrees F.

A few materials, other than those listed in Table IV, were used as test specimens in later work by Babcock and Wilcox Company. These included nickel, Inconel and Monel, as well as many of the same materials of Table IV which had been both spray calorized and pack calorized. Due to the fact that the test specimens were placed in an operating unit, temperatures and gaseous atmospheres were not constant throughout the test periods. Thus, the tests were not made under carefully controlled conditions. Nevertheless, the variety of materials which were deleteriously affected by gaseous atmospheres containing carbon monoxide at temperatures ranging from about 700 to 1700° C. was clearly demonstrated by these results.

After analyzing test results, described above, some of the opinions formed by the Babcock and Wilcox Company were as follows:

> In summary, the attack was relatively light in the high-temperature zone (above about 1650 F) and ceased below about 900 F, but was severe and rapid at the intermediate temperatures....
>
> The over-all evaluation of the materials revealed that those which suffered the least attack were all materials which resist

carburization, that is, nickel, Monel, Inconel, 27Cr stainless, copper, and pack-calorized stainless steel....*

The observations made during the examination of the affected metal parts and test specimens led to the conclusion that the following factors may have been involved in the wastage phenomenon:

(1) Cycling Temperature-Oxidation. Oxidation alone, observed only at the higher temperatures below the water-cooled baffle, appears to have been a minor cause. It manifested itself in the form of pits.

(2) Cycling Carburization and Oxidation. This could have caused a "dusting" of metallic particles, possibly facilitated by thermal stresses due to sootblowing and by abrasion by particles in the gas stream.

(3) Cycling Oxidation and Reduction. It appears to be possible that surface oxide formed during sootblowing with steam was reduced to iron and graphite during the subsequent off-cycle. This possibility is supported by the metallographically found presence of metal particles in a graphitic-appearing deposit as well as by X-ray diffraction identification of the presence of graphitic carbon and traces of iron-graphite (FeC) on one of the affected soot blower elements.

(4) Partial conversion of the outermost surface to solid carbide by continuous carburization and flaking off of the brittle layer.*

The cyclic conditions, mentioned above, appear to have been a result of periodic momentary shut down of the operating unit for the purpose of cleaning, or sootblowing, by steam.

Experience of M. W. Kellog Company (22).--The M. W. Kellogg Company reported on an experience of rather severe corrosion in a hydrocarbon synthesis plant. This plant was used for synthesizing gasoline and related hydrocarbons from coal. Severe corrosion was experienced in parts

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*Refer to Paper No. 15 presented at Fifteenth Annual Conference of National Association of Corrosion Engineers, page 15.

of the system where the materials of construction were of the stainless steel class. Temperatures were of the order of 800 to 1300° F. and gas compositions were of the following approximate two ranges.

	Feed Gas	Product Gas
% H_2	35.0-48.0	47.0-48.0
% CO	13.0-20.0	14.0-17.0
% CO_2	0.8-3.0	5.0-7.5
% CH_4	10.0-18.0	4.0-6.0
% C_2-C_4	0.0-3.0	0.0
% N_2	0.5-4.0	0.5-4.0
% Steam	20.0-24.0	19.0-30.0

Corrosive effects were first observed on AISI Type 310 stainless steel, where temperatures were of the order of 1200 to 1300° F., and the atmosphere was of the feed gas composition given above. These effects were observed after about 3000 hours service. Later, similar observations were made on Type 310 stainless steel in a temperature zone of 900 to 1000° F. and a feed gas composition without steam. Although Type 310 stainless steel was the only metal which had been attacked before the writing of the report cited here, other stainless steels were found to be attacked later. The author of the paper pointed this out at the presentation given at the 1959 Annual Conference of National Association of Corrosion Engineers.

The corrosion was generally of a localized, or pitting form. Microscopic examination, supported by chemical analysis, indicated

localized carburization in the attacked zones. Diffusion of carbon into the metal was indicated to be along grain boundaries.

Miscellaneous Related Works and Comments on Cited Literature.--Various other works have touched, at least indirectly, on matters pertinent to the work undertaken in the present research. For example, the work of Berry, Ames and Snow (23) indicated that small amounts of ammonia or sulfur tend to inhibit the decomposition rate of carbon monoxide. On the other hand, they indicated that the presence of hydrogen tends to enhance the rate of carbon monoxide decomposition. These authors stated that carbon (from CO decomposition) destructively affected ceramic materials containing iron, iron oxide and other materials which catalyze carbon monoxide decomposition.

Considerably in contrast to the subject under consideration here is the destruction of a flake graphite cast iron reported by Billington and Woodfine (24). Here, a flake graphite cast iron was catastrophically corroded by carbon dioxide (with small amounts of carbon monoxide) at temperatures ranging from 375 to 525° C. This corrosion process was apparently due to an oxidation mechanism. This reference serves to illustrate the complexity of reactions of gases containing carbon on metals like iron at temperatures near 1000° F.

The work of Leidheiser and Gwathmey (16) and Kehrer and Leidheiser (17), described above, had indicated possible removal of nickel from single crystals of nickel which were subjected to carbon monoxide at 550° C. This was suggested by a statement of Leidheiser and Gwathmey (16) that chemical analysis of carbonaceous deposits on nickel foil showed

11.01 weight per cent nickel. Further, Kehrer and Leidheiser (17) stated that carbon had deposited in small pits of approximately hemispherical shape on flat single crystals. These two statements suggested that possibly the pits were the result of loss of metal during exposure to carbon monoxide. Contradictory to this argument, however, was the statement made by Kehrer and Leidheiser (17) that X-ray diffraction analysis did not support the chemical analysis reported by Leidheiser and Gwathmey, above. To resolve this matter, Kehrer and Leidheiser were contacted by personal correspondence. It was the opinion of Mr. Leidheiser that the pits were the result of electrolytic polishing preparatory to exposure to carbon monoxide. Further, he felt that the destructive effects of carbon monoxide on the nickel crystals were likely quite small, if any at all.

CHAPTER IV

EXPERIMENTAL APPARATUS, PROCEDURES AND RESULTS

The equipment used for experimentation in this research work can be classified broadly as (a) the reaction, or exposure, system and (b) analytical apparatus. Generally, the analytical equipment was standard apparatus, or was equipment which has been well described in technical literature. No analytical equipment is described in detail in this chapter.

Apparatus Description.--Basically, the exposure system provides facilities for exposing small metal samples to high purity carbon monoxide at temperatures near 1000° F. The exposure zone is approximately 3/8 inch in diameter and is two feet long. Temperatures in this zone can be controlled to within about ± 10° F. for periods of the order of 100 hours. Control of temperatures is accomplished by the use of commercial automatic instruments. Temperature uniformity and narrow control range are provided by the use of a fluidized-solids heat transfer medium. This medium surrounds the exposure zone. The equipment was operated satisfactorily at temperatures up to 1100° F.

Experimental carbon monoxide was high purity commercial gas. The manufacturing specifications on this gas require 99.5 volume per cent minimum purity. Impurities when manufactured are nitrogen and oxygen in about the same relative proportion as in air. It was purchased from the

Matheson Company, Incorporated, East Rutherford, New Jersey. The experimental apparatus provides facilities for use of the carbon monoxide supplied in high pressure cylinders. The cylinders contained about 100 cubic feet of gas when measured at atmospheric conditions. Also provided in the exposure system is gas metering and flow rate control equipment. The gas was fed to the reactor at rates of about 0.3-1.0 cubic feet (at atmospheric conditions) per hour. Variations in gas rates, due to metering and control, were about $\pm$ 10 per cent. A thermal purification unit was provided in the carbon monoxide system and was operated at a controlled temperature of 700° F. This purification unit served to decompose iron carbonyls which potentially form in the gas cylinders, upon long standing. Auxiliary gas metering and control facilities were installed. Although not used in the presently discussed experimental program, these facilities were installed for potential use of diluent gas, such as nitrogen, or secondary exposure gas, such as hydrogen.

Besides the facilities discussed above, other equipment was used for (a) collection of entrained solid matter in the effluent carbon monoxide, and (b) collection and analysis of gas samples.

Construction material, which was used for the exposure system, was AISI Type 446 stainless steel. This material was used throughout the entire system from the carbon monoxide purification unit to the disposal zone. AISI Type 446 steel (25) was suggested to possess high corrosion resistance to gases containing carbon at temperatures near 1000° F. However, selection of this material was not straight forward

and without confusing factors. Nevertheless, the material was used and proved to be satisfactory for the experimentation. AISI Type 446 steel is a ferritic stainless steel and has a nominal composition of 23 to 27 weight per cent chromium. Except for minor impurities (less than 3% total), the balance of this alloy is iron.

A schematic diagram of the experimental exposure system is shown in Figure 3. To illustrate the manner in which this equipment was used, a brief description of the normal flow path of the experimental carbon monoxide follows.

The carbon monoxide comes from high pressure cylinders (at A in the diagram) and passes through a manifold to the CO rotameter (at B). The rate is controlled by a needle valve and a pressure regulating valve on the gas cylinder. After the rotameter, the carbon monoxide goes through a purification unit which is called the "CO Pretreater" (at C) for the purpose of thermally decomposing any iron carbonyl which may have formed in the cylinder. Following purification, the gas passes through a preheating coil in the fluidized-solids temperature bath. This preheating coil is not shown in the diagram in order to reduce complexity. After preheating, the experimental gas goes into the reactor (at D) and passes over the metal specimen under study. Next, the effluent gas is cooled in a water jacketed cooler (at E). The cooled gas then goes through a dust collector (at F) for entrapping any solid material carried over from the reactor. Following this, the gas is normally discarded through a vent. Periodically, the effluent gas is sampled and analyzed.

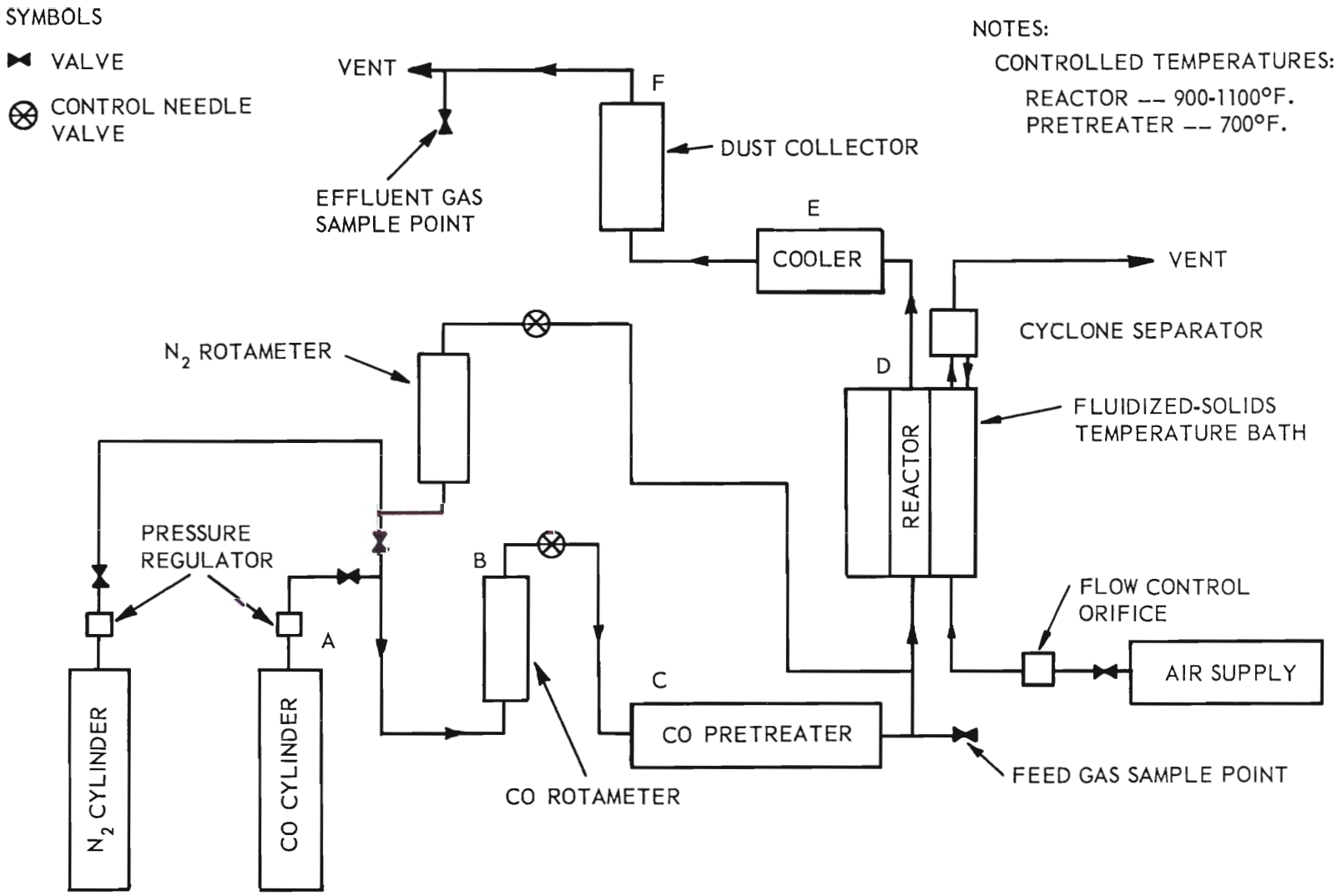


Figure 3. Schematic Diagram of Experimental Apparatus.

Various auxiliary facilities are schematically shown in Figure 3. These include the dry nitrogen system and the fluidized-solids temperature control system. Dry nitrogen is used as a flush gas.

A detailed description of the experimental apparatus is given in Appendix A, page 98. This description includes detailed information on:

(1) Design basis.

(2) Description of equipment.

(3) Materials of construction.

(4) Design calculations.

(5) Calibrations and engineering test results.

Experimental Procedure.--The experimental procedure followed in this work was as follows. After the desired reactor and CO pretreater temperatures were obtained, the feed carbon monoxide was tested for purity. Wire specimens were placed in the hot reactor and allowed to heat soak for about one hour in a nitrogen atmosphere. These wire specimens had previously been cleaned and weighed. Following the heat soaking, carbon monoxide flow was started through the system as discussed above. Periodically, various experimental information was recorded. A sample experimental data sheet is given in Table V, page 47, which shows the type of data recorded. After the desired exposure time had been obtained, the carbon monoxide flow was stopped. Then, dry nitrogen was flushed through the system. Following the nitrogen flush, the wire specimens were carefully removed from the hot reactor and placed in a dessicator. The exposed wires were then weighed and again placed in a dessicator awaiting further analysis.

A detailed outline of the experimental procedure is also given in Appendix A following the description of equipment.

Experimental Results in General.--The experimentation associated with this research program involved three types of metals. They were commercially pure nickel, Inconel and AISI Type 304 stainless steel. All metal specimens were in the form of wires and were either 0.01 inches in diameter (pure nickel and Type 304 stainless steel) or 0.008 inches in diameter (Inconel). The nickel and stainless steel specimens used were about 100 feet long, and the Inconel specimens were about 130 feet long. All metal samples were prepared for exposure to carbon monoxide as outlined in the sample and apparatus preparation description on page 119. Typical chemical compositions and metallurgical histories of these three metals are given in Appendix E, page 130. Chemical analyses of the experimental wires for principal constituents gave the following results:

	Chemical Analysis* of Wires, weight per cent.					
Material	Fe	Cr	Ni	Mn	Si	C
Nickel	0.09	--	99.5	0.25	--	0.12
Inconel	7.7	16.0	75.2	0.20	0.18	0.09
Type 304 Steel	68.5**	19.3	10.3	1.49	0.36	0.05

In all experiments, the metal specimens were subjected to high purity carbon monoxide, at various controlled temperatures ranging from about

*Chemical analyses were made at Atlantic Steel Company, Atlanta, Georgia.

**This value is assumed as balance, which is common practice.

920° to 1100° F. Carbon monoxide exposure times ranged from 4 to 120 hours, but typically, exposures were for 16 hours.

During the various experimental runs, normal variations in the controlled exposure temperatures were of the order of ± 5° F. Although unusual, in some instances, maximum recorded temperatures were as much as 30° F. higher than minimum recorded temperatures. Variations in controlled experimental carbon monoxide rates were of the order of ± 10 per cent.

In the early stages of the experimental program, pure nickel and Inconel were investigated. However, the reactivity of these materials with carbon monoxide was found to be considerably lower than that of stainless steel. Because of the higher reactivity, extensive experimentation was done on the stainless steel. In the following pages, results of the work on stainless steel will be presented first, and the results on pure nickel and Inconel will be given in detail afterwards.

Experimental Results on AISI Type 304 Stainless Steel.--Type 304 stainless steel wire specimens were exposed to carbon monoxide in twenty-one experiments. In seventeen of these experiments, exposure times were 16 hours. Two experiments were made with 32 hours exposure and one with 120 hours exposure. The remaining experiment of this set was made with a carbon monoxide exposure time of about 46 hours. However, electrical heaters burned out and the air supply compressor failed near the end of this experiment. Consequently, satisfactory experimental results were obtained with exposure times of 16, 32 or 120 hours, only. Temperatures

ranged from about 920° to 1100° F. Carbon monoxide rates were normally about one standard cubic foot (measured at 14.7 p.s.i.a. and 60° F.) per hour, but six experiments, or runs, were made at about 0.3 standard cubic foot per hour. In every experiment, carbonaceous deposits on the wire surfaces resulted in increased weights of the wire samples during exposure. Over the ranges of variables studied, carbonaceous weight gains tended to increase with temperature and exposure time. Weight increases varied from about zero at the lower temperatures and exposure time to about two per cent at the higher temperatures and/or exposure times. The data suggested that about two per cent weight gain of the wire specimens may have been the upper limit. Chemical analyses of two different samples of the carbonaceous surface deposits indicated metal contents (only analyzed for Fe, Cr, and Ni) to be:

Carbon	80.0
Iron	7.5 - 12.3 weight per cent
Chromium	0.05 - 0.3 weight per cent
Nickel	1.0 - 4.57 weight per cent

The surface deposits were ferro-magnetic. X-ray fluorescence analyses, at least semi-quantitatively, supported these chemical analyses.

Positive identification of the structure of the metallic components in the carbonaceous surface deposits was not possible by the use of X-ray diffraction analysis. Chemical analyses of the surface deposits indicated them to be about eighty weight per cent carbon, and X-ray diffraction analysis suggested that this was predominantly graphitic. Further, X-ray

diffraction suggested the possibility of free nickel and iron or iron-nickel alloy-like materials in the surface deposits. The diffraction analyses, however, were quite inconclusive. One could not exclude the possibility of many other materials, such as carbides, etc., in the surface deposits from the X-ray diffraction work. The principal reasons that X-ray diffraction analyses were inconclusive were:

1. All the metals - α Fe, Cr and Ni - as well as the carbides - $Cr_{23}C_6$, Fe_3C, $Fe_{20}C_9$, Ni_3C - and iron graphite have highest diffraction intensities at d values - between 2.01 and 2.05 Å.
2. The stronger diffraction lines, in general, indicated face centered cubic structures, such as from nickel and nickel alloys, or body centered cubic structures, such as from αFe or low Ni-αFe alloys. However, since most of the analytical work employed powder camera techniques, broad diffraction lines at d values near 2.01 - 2.05 could not be resolved into multiple components, as was probably the case.
3. Some faint diffraction lines could not be identified with any proposed structure.

Metallurgical examination of cross-sections of the wire specimens indicated, at least in part, the attack on the metal was along grain boundaries in localized areas. Chemical analysis of wire specimens, which had been cleaned of surface deposits, showed that appreciable carbon had penetrated into them. The amount of carbon penetration tended to increase with increasing amounts of surface deposition and

amounted to about 0.6 weight per cent in a very severe case. The original carbon content of the stainless steel wires was about 0.05 weight per cent.

Microscopic and metallurgical examination of cross-sections of the exposed wires suggested the possibility that individual grains of the metal were mechanically forced from the surfaces of the wires due to intergranular carbon or carbide formations. If this was the case, the extent of this process (in the exposure times involved) must have been relatively small compared to other processes which took place and resulted in metal transfer into the surface deposits. This statement is supported by chemical and X-ray fluorescence analyses of the deposits and electron microprobe analyses of individual grains of metal. These individual grains of metal were nearly at the stage of being removed by the suggested mechanical process. Chemical and fluorescence analyses showed that the relative amounts of chromium (to iron and nickel) in the deposits were quite low compared to that in the original wire specimens. On the other hand, electron micro-probe analysis of the individual grains, still at the wire surface but clearly indicated to be progressing towards removal, showed that the relative chromium contents were near the same as that of the original wire specimens. Thus, mechanical removal of individual grains does not appear to have been a major source of metal wastage, at these exposure conditions. Microscopic examination of the surface deposits revealed metallic-like particles enmeshed in the deposits. These particles were, in many cases, of the same order of size as individual grains of the original wires. A very limited electron micro-probe analysis of a few of these particles revealed appreciable amounts of iron, a small amount of nickel and no chromium.

Limited testing indicated that the stainless steel wires were not sensitized to intergranular attack by heat treatments comparable to the exposure conditions (time and temperature) which were used in this experimental program.

Three experiments were made in which tests were made for carbonyls in the carbon monoxide after exposure. Results of these tests indicated that if carbonyls of iron and nickel were present in the effluent carbon monoxide after exposure, the amounts were extremely small.

Experimental Results in Detail.--As stated earlier, the stainless steel wires were 0.01 inches in diameter. Microscopic examination revealed that these wires were very nearly circular in cross section but had very shallow surface irregularities resulting from the drawing dies. These irregularities were in the form of ridges and grooves (of the order of 0.0001 inches deep) which occurred alternately at intervals of about 0.0001 to 0.0005 inches and ran longitudinally along the wires. For all experiments on stainless steel, specimens were prepared by wrapping about 100 feet of the wires to form a bundle about 12 inches long and $\frac{1}{4}$ inch in diameter (very loosely packed). The samples were cleaned, dried and weighed as outlined on page 119.

For sixteen hours exposure times, the weight gains (due to carbonaceous deposits) of the stainless steel specimens increased with temperature for the range of 920° to 1100° F. Figure 4 is a graph of weight gains as a function of temperature for the 16 hour runs on stainless steel. Clearly, Figure 4 shows that weight gains tend to increase with temperature. This trend is particularly noticeable above

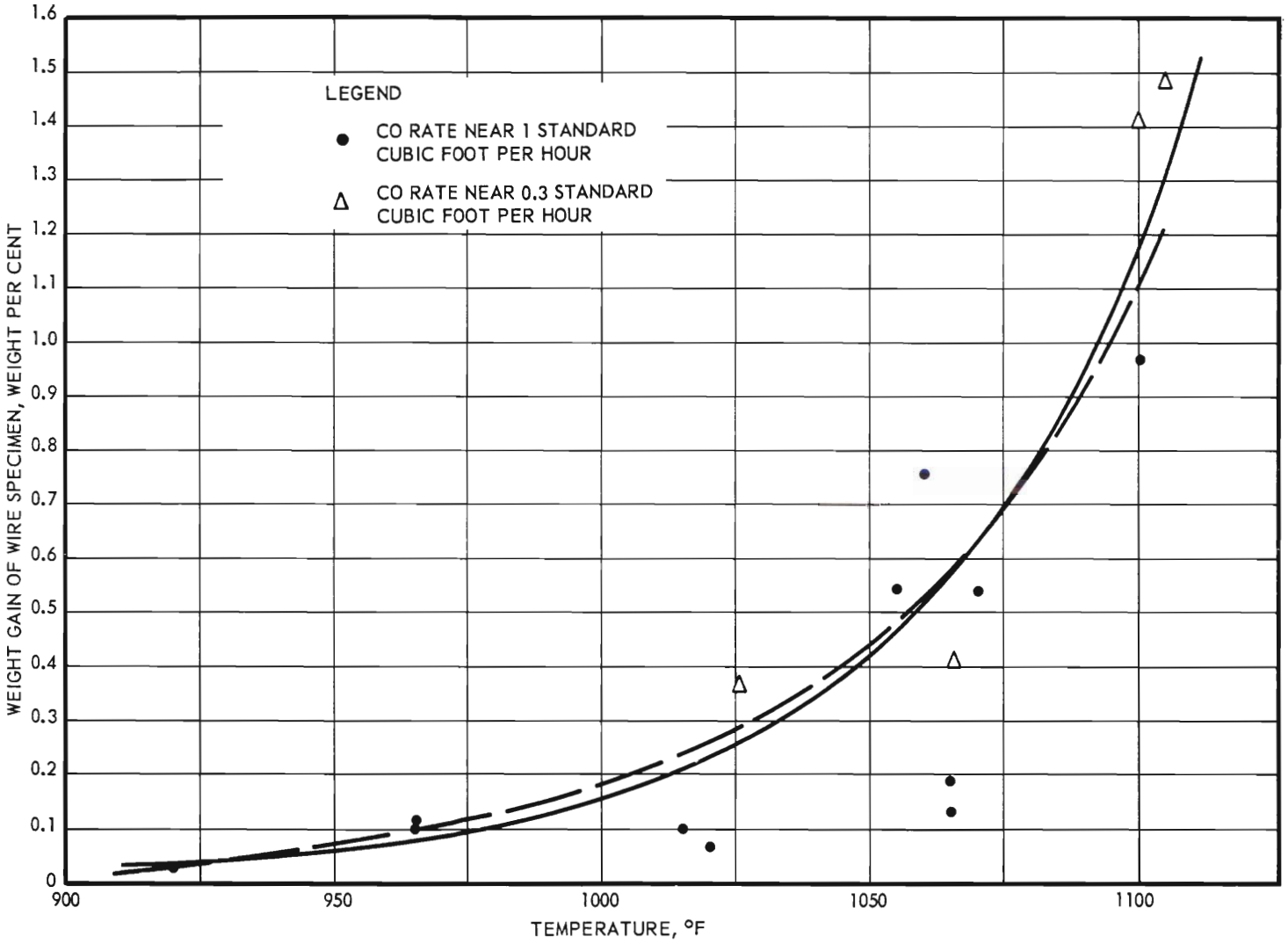


Figure 4. Weight Gains of Type 304 Stainless Steel Wire Specimens Exposed to Carbon Monoxide Versus Temperature.

about 1020° F. Figure 4 includes the results of fifteen of the runs at 16 hours exposure time. The solid curve was drawn in graphically rather than from analytic determinations. Selected data (Runs 12, 13, 18, 19, 20, 21, 25, 27, 29, 30, and 31) were used to prepare the broken curve by use of the methods of least squares curve fitting. For this analytical curve fitting, it was assumed that the kinetically controlled process obeyed an Arrhenius relationship, i.e., the rate constant is proportional to exponential -b/T, where b is the activation energy divided by the gas constant, and T is the absolute temperature. For the details of these calculations, see the analysis of data on pages 79 and 80 . The Arrhenius relation did not fit the data too well, probably due to the variability of the system. However, b was calculated to be about 40, 150 ($\pm$ 11,700) degrees Rankine. This corresponds to an activation energy of approximately 44,300 calories/mole.

An example data sheet which was prepared during Run 30 is shown in Table V. These data describe the exposure conditions for a sample of stainless steel for the nominal conditions: 16 hours exposure at 1100° F. to one standard cubic foot per hour of carbon monoxide at one atmosphere pressure. Temperature recorder-controller charts showing the temperatures of the reactor and the carbon monoxide pretreater during Run 30 are given in Figure 5. Average results describing exposure conditions for all other experiments on stainless steel are given in Tables B-I and B-II, pages 122 and 123.

Experimental Results on Pure Nickel and Inconel.--Limited data were obtained on nickel and Inconel. As explained earlier, emphasis was placed

TABLE V

EXAMPLE EXPERIMENTAL DATA SHEET

DATE: 9/15/59 METAL DUSTING EXPERIMENT NUMBER 30 MATERIAL: 10 MIL DIAMETER 304 STAINLESS STEEL WIRE

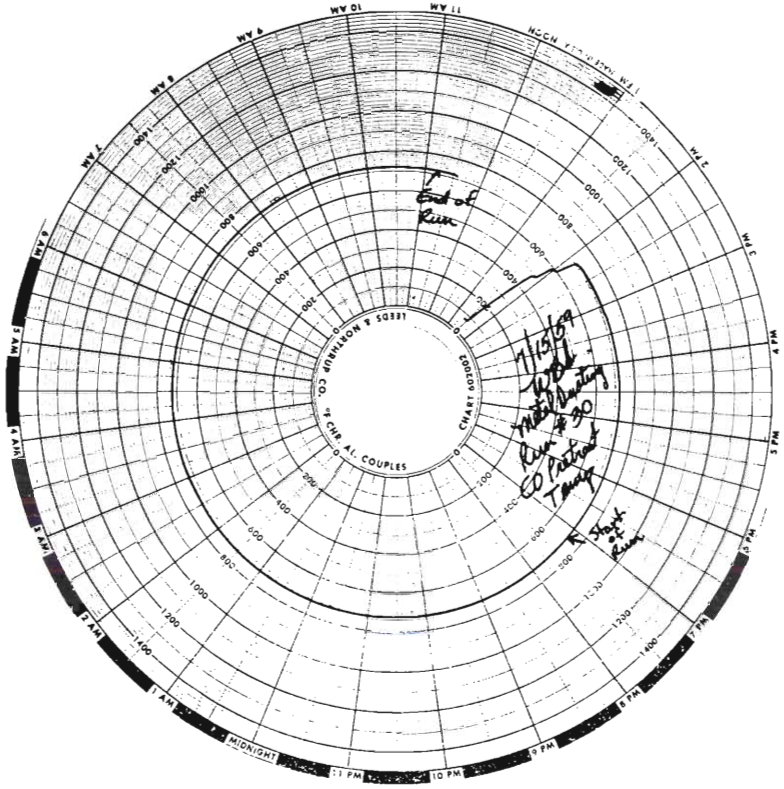
NOMINAL CONDITIONS: 12 GRAMS 10 MIL 304 STAINLESS WIRE, 1 SCFH* CO, 1100°F., 16 HOURS, 1 ATM. ABSOLUTE

TIME	REACTION TEMP., °F.	PRETREAT TEMP., °F.	REACTOR PRESSURE, p.s.i.g.	FLUIDIZATION AIR PRESSURE, p.s.i.g.	ROTAMETER		CO CYL. PRESSURE, p.s.i.g.	ORSAT ANALYSIS**			REMARKS AND MISCELLANEOUS
					PRESSURE, p.s.i.g.	SCALE		VOLUME % CO_2	VOLUME % O_2	VOLUME % CO	
7:15 P.M.	1100	710	0	60	56	1.01	750	---	---	---	(1) INITIAL SAMPLE SIZE:
8:15 P.M.	1100	710	0	75	56	1.01	740	0.6	0.0	97.8	12.8045 GRAMS.
9:15 P.M.	1100	710	0	75	58	1.01	730	0.6	0.0	98.4	(2) SAMPLE PLACED IN
10:15 P.M.	1100	710	0	70	59	1.00	720	0.5	0.0	98.6	REACTOR 5:00 P.M. 9/15/59
9/16/59											(3) CO FEED ANALYSIS 7:00
8:30 A.M.	1100	710	0	66	58	0.96	610	0.4	0.0	99.0	P.M.: CO_2 0.2, CO 98.4
9:30 A.M.	1100	710	0	55	59	0.99	600	0.4	0.0	98.6	(4) CO TO REACTOR 7:10 P.M.
11:05 A.M.	1100	710	0	62	58	0.98	590	0.4	0.0	98.4	(5) CO OUT, N_2 FLUSH IN
											11:10 A.M. 9/16/59

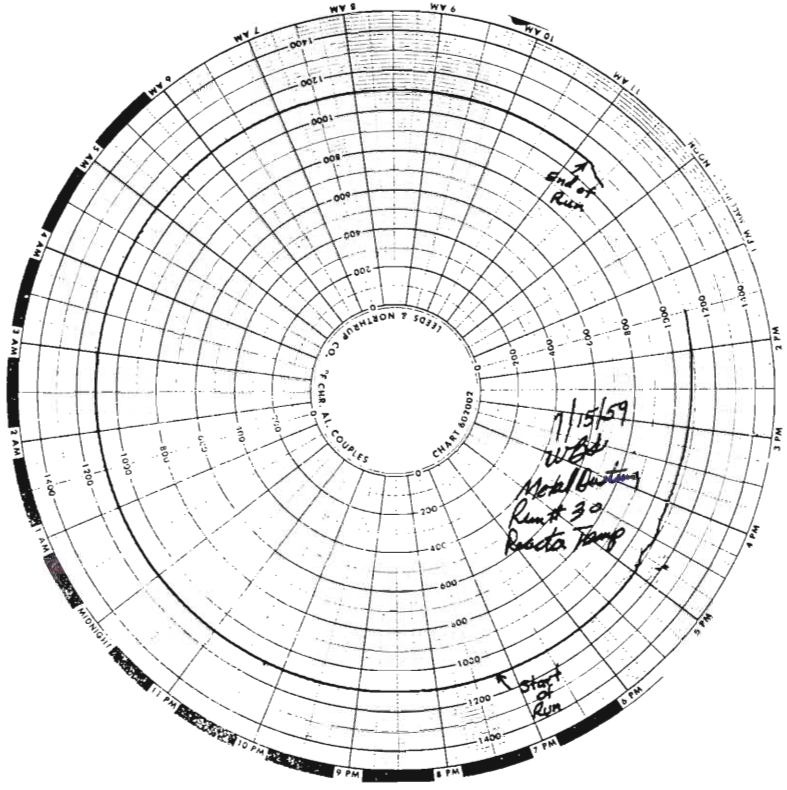
FINAL SAMPLE WEIGHT: 12.9290 GRAMS. WEIGHT CHANGE: 0.1245 GRAMS (0.971 %).

* Standard engineering symbol for standard cubic feet (measured at 14.7 p.s.i.a. and 60°F.) per hour.

**At these levels of measurements, these analyses are quite qualitative. The burettes used in this apparatus can only be read accurately to 0.2 ml. (0.2 volume % on 100 c.c. sample). Further, the CO analysis is probably of poorer accuracy than this because of mainpulation difficulties associated with requiring almost complete adsorption of this component in the experimental gas. For these reasons, the Orsat analyses were made, merely as a control measure, to indicate reactivity of the system.



CARBON MONOXIDE PRETREATER TEMPERATURE, °F
METAL DUSTING RUN NUMBER 30



REACTOR TEMPERATURE, °F
METAL DUSTING RUN NUMBER 30

Figure 5. Example Temperature Recorder Controller Charts.

on the Type 304 stainless steel because of its higher reactivity with carbon monoxide. For example, the following table shows the weight gains obtained for these three materials upon exposure to carbon monoxide at three different temperatures. Except where noted otherwise, carbon monoxide exposure times were 16 hours.

Table VI

Carbonaceous Weight Gain Comparisons for Nickel, Inconel and AISI Type 304 Stainless Steel

Material	Weight Gains, grams/hour/foot^2, at Indicated Temperatures.		
	1020° F.	1065° F.	1100° F.
Nickel	0.0007*	0.0033**	0.0011
Inconel	0.0022	0.0012	0.0041
Type 304 Steel***	0.0068	0.0168	0.0351

*4 hours exposure to carbon monoxide at 1015° F.

**8 hours exposure to carbon monoxide.

***Values calculated from solid curve of Figure 4.

Data from the nickel and Inconel experiments were obtained similar to that shown in Table V and Figure 5, pages 47 and 48. Average results from the nickel and Inconel experiments are given in Table D-I, page 129.

Analytical Results.--Some analyses of the exposed metal specimens were done by use of the following techniques:

1. Chemical.
2. Electron micro-probe.

3. Metallurgical.
4. Microscopic (optical).
5. X-ray diffraction.
6. X-ray fluorescence.

Chemical Analysis.--Chemical analyses were made on two different surface deposit samples (for iron, nickel, chromium and carbon), five different stainless steel wire specimens (for carbon), as received wires as well as on one cold trap (-80° C.) condensate sample taken from the carbon monoxide after exposure (32 hour condensate collection). A very large number of Orsat analyses were made on the "as received" and effluent carbon monoxide. No chemical analyses were made on exposed Inconel and nickel specimens.

One of the surface deposit samples examined was made up of about equal amounts of material from two different runs. Exposure conditions for these runs were 120 hours at 1065° F. and 32 hours at 1060° F.

The wire specimens, which were analyzed for carbon penetration, were prepared by removing all surface deposits, rubbing the surface of the wires with 3/0 emery paper and wiping clean to remove surface carbon. This cleaning of the wire specimens was done in order to estimate the amount of carbon penetration into the main body of the wires. Results of the chemical analyses of the surface deposits and the wire specimens are given in Table VII.

During Runs 28, 2a and 3a, the effluent carbon monoxide from the reactor was passed through a cold trap. This trap was maintained at about -80° C. by use of acetone and Dry-ice as coolant. A small amount

Table VII

Chemical Analyses of Carbonaceous Surface Deposits on Type 304 Stainless Steel Wires

Run Number	Sample Type	Exposure Conditions: Time, hours	Exposure Conditions: Temperature, °F.	Exposure Conditions: CO Rate, SCFH[+]	Wire Sample Weight Gain, weight %	Chemical Composition, weight per cent: Fe	Cr	Ni	C
24	Deposit	32	1060	0.28	2.13	7.5	0.05	1.0	80 (79[*])
26	Deposit	120	1065	0.92	2.11				
25	Deposit	16	1100	0.29	1.41	12.3	0.3	4.57	--
--	Wire	None	None	None	--	--	--	--	0.05[*]
20	Wire	16	920	0.95	0.03	--	--	--	0.08[*]
12	Wire	16	1020	0.97	0.15	--	--	--	0.14[*]
27	Wire	16	1105	0.30	1.49	--	--	--	0.63[*]
26	Wire	120	1065	0.92	2.11	--	--	--	0.68[*]

[*]Analyses made at chemical control laboratory of the Atlantic Steel Company, Atlanta, Georgia. All other chemical analyses were made by Law and Company, Atlanta, Georgia.

[+]Standard cubic feet (measured at 14.7 p.s.i.a. and 60° F.) per hour.

of icy-solid condensate was formed in the trap during each of these experiments. After each run was complete, the trap was removed from the coolant. Upon warming towards room temperature, the icy-solid condensate melted and formed a colorless liquid. The quantity of liquid was estimated to be 0.5 - 1 cubic centimeter for Runs 28 and 2a. The estimated liquid volume for Run 3a was 0.1 - 0.3 cubic centimeter. Run 28 was made under erratic experimental conditions and hence, there was no analytical treatment of the condensate. Reactor effluent gas was passed through the cold trap in Run 3a to confirm the amount of condensate collected in Run 2a. No analytical treatment was performed on the condensate from Run 3a.

Qualitative analysis for iron, nickel and chromium was performed on the cold trap condensate sample from Run 2a. Little, if any, of these materials was present. However, faint traces of iron and nickel could not be excluded by the tests. The analysis made use of bromine for decomposition of possible carbonyls. Standard reagents were used for qualitative tests for iron, nickel and chromium. Ammonia was added to the brominated test liquid for precipitation of ferric hydroxide (brown solid). Then the solution was boiled down to a volume of about 2 cubic centimeters. The ammonia also used up excess bromine. At this point, if the solution had been pale yellow, chromium in the form of chromate ions would have been indicated. Dimethyl glyoxime was added to the ammoniacal test solution for precipitation of the red colored complex of nickel. All these tests were negative in the normal test solution volumes. However, the solution (about 2 cubic centimeters) containing the dimethyl glyoxime was boiled down to a volume of about $\frac{1}{2}$ cubic

centimeter. At the beginning of this boiling, a little color began to develop. When the $\frac{1}{2}$ cubic centimeter volume was obtained, the solution was a pale brownish-pink color. Hence, faint traces of iron and nickel could not be excluded by the tests. Since this cold trap condensate sample was collected over a period of thirty-two hours, the amount of nickel and iron in the effluent carbon monoxide from the reactor was indicated to be very small.

Presumably, the major portion of the cold trap condensate from Runs 28, 2a and 3a was water. If it was water, estimates for Run 2a showed that the amount in the carbon monoxide was about 0.1 volume per cent. This same order of magnitude is also true for the "water content" of the effluent carbon monoxide in Run 3a.

Cold trap operation at -80° C. is satisfactory for condensing rather low concentrations of iron and nickel carbonyls. However, significant amounts of these carbonyls can pass through the trap uncondensed. For example, $Ni(CO)_4$ concentrations of the order of 0.01 volume per cent will pass through a cold trap maintained at -80° C. Since $Fe(CO)_5$ is similar in volatility to $Ni(CO)_4$, concentrations of $Fe(CO)_5$ of the order of 0.01 volume per cent will also pass through a cold trap maintained at -80° C. Although such concentrations are low, the quantity of equivalent metal to these concentrations reaches significance in terms of quantities of metal involved in corrosion processes. For this reason, if extensive future research is done to explore gas phase reaction products formed from carbon monoxide with metals, such as studied in this work, it is suggested that cold trap operations be carried out near -120° C.

X-ray Fluorescence Analyses.--X-ray fluorescence analyses were made on three surface deposit samples and on two types of wire specimens. This information was considered semi-quantitative, but it definitely supported the chemical analyses of the surface deposits discussed on page 50. Further, tests on "as received" samples of the stainless steel wires and samples of cleaned wires from Run 25 showed that the exposed wires had higher relative contents of chromium than the "as received" wires. This was compatible with the chemical analyses of the surface deposits which indicated low chromium contents (relative to iron and nickel) of the deposits. The fluorescence data ($K\alpha$ peaks of Fe, Cr and Ni) were used to approximate the composition of the surface of the sample from Run 25. Results of these tests are as follows:

Approximate Composition by X-ray Fluorescence

	Run 25	As Received (Assumed)
Iron	67.6 weight per cent	68.5 weight per cent
Chromium	20.4 weight per cent	19.3 weight per cent
Nickel	10.1 weight per cent	10.3 weight per cent
Ni/Fe Ratio	0.1494	0.1504

For these analyses, 15 wires were used for each X-ray specimen. Four "as received" and three Run 25 exposed wire specimens were analyzed. Three radiation counts (Geiger tube counts per second) were measured at each of the $K\alpha$ peaks for iron, nickel and chromium, on every specimen. There were statistical variations in the results, but in no case were there inconsistencies. That is, the relative amounts of chromium (to

iron and nickel) in the exposed wires were consistently higher than in the "as received" wires. The above compositions are based on averages of all the analyses. The method of calculation involved the following assumptions:

1. Composition of the "as received" wires.
2. Radiation counts proportional to atomic percentages.
3. Fluorescence interaction effects in the exposed wires proportional to those in the "as received" wires.
4. Combined total of 98.1 weight per cent Fe, Cr, and Ni in both type wires.

Of course, the calculations are rough approximations. And, the X-rays do not penetrate the wires more than distances of the order of 0.001 inch. Thus, slightly higher chromium contents in the exposed wire surface areas was concluded. Even though slight, the chromium composition differences were nevertheless significant.

X-ray Diffraction Analyses.--X-ray diffraction analyses were made on the untreated, or "as received", nickel, Inconel and stainless steel wires. Also, a number of analyses were made on treated wire specimens and surface deposits. The differences in diffraction patterns for treated specimens and untreated specimens were, in general, very slight and, indeed, not enough to reach definite conclusions. At most, the presence of graphitic carbon was indicated on the treated wire specimens, based on the appearance of the most intense diffraction line for graphite ($d = 3.37$ Å). On the other hand, some surface deposit analyses suggested the presence of materials other than graphite. Appendix C, pages 124-128,

shows the results of the more promising diffraction patterns. Included in Appendix C are patterns of the untreated wire specimens. Only the more intense lines (I/I_o greater than about 10) are reported in Appendix C. To illustrate the extent of the numbers of faint diffraction pattern lines, two detailed patterns are given in Table VIII. They are representative of the more complicated X-ray patterns obtained.

There were possible differences in the less intense diffraction lines for the different specimens. However, extensive study of these patterns did not produce any satisfactorily definite conclusions concerning the source materials for differences in diffraction results. X-ray diffraction information of the American Society for Testing Materials (26) was used in the study of the various experimental diffraction patterns. In particular, on the carbonaceous surface deposits, no positive identification of the following metallic materials could be made: Cr_3C_2, Cr_7C_3, $Cr_{23}C_6$, Cr, "FeC", Fe_2C, Fe_3C, $Fe_{20}C_9$, αFe, Ni_3C and Ni. Especially confusing in these analyses, however, was the fact that nearly all the above materials have very strong diffraction line intensities at d values between about 2.00 and 2.06 Å. The best analysis was considered to be that of the diffractometer pattern for a surface deposit from Run 25 in Appendix C (Analysis 9). The strong intensity at d = 3.37 Å in this analysis suggests graphitic carbon. The strong intensities at d = 2.02 -2.06 Å (I/I_o = 75) and at 1.78 Å (I/I_o = 28) suggests nickel or nickel alloy-like material. The strong intensity at d - 2.02 Å (I/I_o = 100), supported by the weaker intensities at d = 1.44 and 1.16 Å (I/I_o = 10) suggests αFe or a body centered iron-nickel alloy type material.

Table VIII

Detailed Results of Complicated X-ray Diffraction Patterns of Carbonaceous Deposits

Run Number: 24/26. Type X-ray Sample: Surface Deposit. Method: Powder Camera.

Radiation: Molybdenum (45 KV, 20 ma). Filter: Zirconium. Exposure: 12 hours.

d:	3.39	2.51	2.40	2.26	2.05	1.97	1.87	1.79	1.70	1.47	1.42	1.33
I:	VS*	P	P	P	VS*	VVW	VW	M*	VW	P	VW	P
d:	1.26	1.22	1.17	1.12	1.08	1.03	1.01	0.91	0.82	0.80	0.77	
I:	W*	VW	W**	VVW	W*	P	P	P	P	P	P	

Run Number: 25. Type X-ray Sample: Surface Deposit. Method: Diffractometer.

Radiation: Molybdenum (45 KV, 20 ma). Filter: Zirconium. Scan: $2\theta = 50°$, $\frac{1}{2}°$/minute.

d:	3.37	2.95	2.74	2.66	2.41	2.06	2.04	2.03	2.02	1.78	1.49	1.47
I/I_o:	72*	12**	9	10**	8		75*		100*	28*	P	8
d:	1.44	1.26	1.22	1.21	1.16	1.15	1.08	1.07	0.85			
I/I_o:	10*	P	9	9	10*	P	8	8	8			

d = lattice spacing, Å. I = intensity. I/I_o = relative intensity. M = medium.

P = possible. S = strong. V = very. W = weak.

*Intensities recorded and structure tentatively identified in Appendix C, pages 124-128.

**Intensities recorded in Appendix C, but structure not tentatively identified.

It may be noticed in Appendix C that X-ray diffraction analyses were not made on surface deposit material from the nickel and Inconel wires, except on the surface of the wires. This was because of the limited quantity of deposited material on all of these specimens. Only by scraping the wires could enough material be obtained from the nickel and Inconel samples. This, of course, would have resulted in scraping surface metal off and hence confusing the analysis even further. Therefore, coated wire specimens were placed directly into the diffraction camera for analysis. In the case of stainless steel samples, sufficient amounts of surface deposits allowed collection of X-ray diffraction samples by merely tapping the wire specimens and collecting the material which fell from the wires. The surface deposits fell from the wires onto clean glossy finish paper. In every case, the entire deposit on the collection paper could be lifted with a small magnet. Nearly all the surface deposit from Run 25 was collected in this manner in order to get sufficient material for an X-ray diffractometer specimen. Although the sample was small compared to most diffractometer specimens, a diffraction trace was obtained. This same specimen was used to estimate crystallite size for the material which was presumably graphite (d = 3.37 Å). This crystallite size was estimated to be about 200 Å. Estimation of crystallite size for the metallic materials (d = 2.02 -2.06) was not possible because of overlap of the diffractometer peaks in this analysis.

Microscopic Examinations.--Various specimens of carbonaceous surface deposits and wires were observed microscopically. Examination showed

a number of metallic-like particles enmeshed in the surface deposits. Figures 6 and 6a show examples of large metallic-like particles in the surface deposits of carbonaceous material. This particular wire specimen is from Run 30. Figure 6, Plate 2 shows a number of rather small particles and one rather large particle in a top view. Figure 6a shows a similar particle in a side view. Since the wire surfaces are not flat, these pictures had to be taken at low magnifications (10X and 25X negatives). Even at these low magnifications, the major portion of the wires are out of focus in order to allow sharper focus on the particles. Also seen in Figure 6 is a reasonably good view of the nature of the carbonaceous deposit.

Attempts were made to quantify the number of particles in the surface deposits. This, of course, was quite difficult to do, but approximate particle counts were made in the following manner. A one inch long wire specimen was carefully taken from the exposed samples of stainless steel wires from Runs 12, 26, 27 and 32, as well as from the "as received" stainless steel wire. These one inch wire specimens were observed microscopically at 40X magnification and the numbers of metallic-like particles on one side of the wires were counted. The wires from Runs 12, 26, and 27 were then tapped and the largest part of the carbonaceous deposits were thus removed from the surface. These wires were again observed and particle counts were made. Finally, particle counts were made on the specimens from Runs 12, 26 and 27 after wiping the wires with lens tissue. Approximate particle sizes were estimated by classing the individual particles as being near a fraction

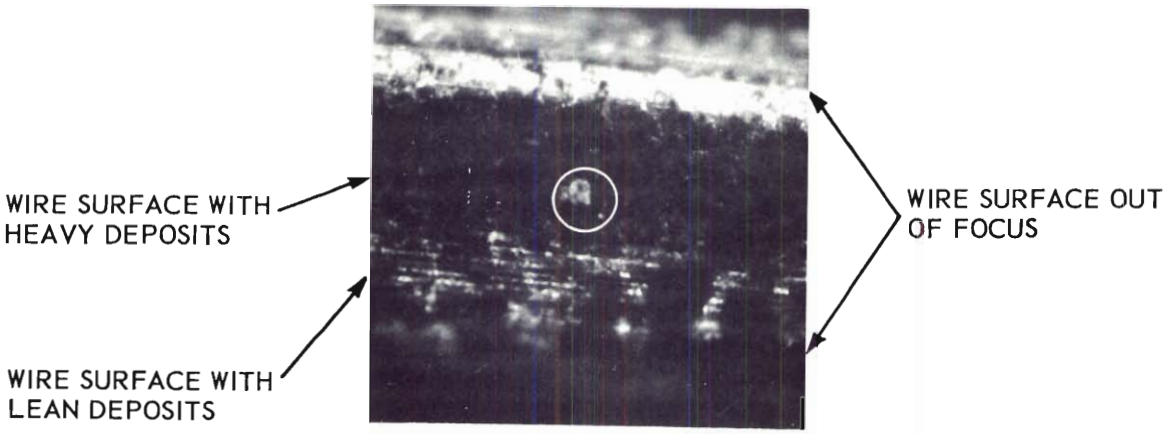


PLATE 1

Example of Large Metal-like Particle (circle) in Carbonaceous Deposits on Surface of Wire from Run 30. Magnification: Enlargement to about 200X from 10X negative. Large Particle on top of wire as viewed in microscope, for photograph.

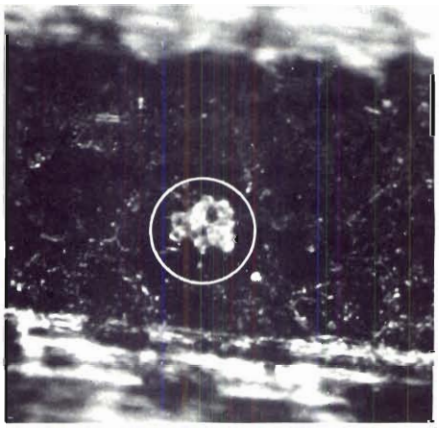


PLATE 2

Same Specimen and View as in Plate 1, above. Enlargement to about 500X (25X negative) showing detail of other smaller metal-like particles in surface deposit.

Figure 6. Examples of Metal-like Particles in Carbonaceous Deposits on Surface of Type 304 Stainless Steel Wires.

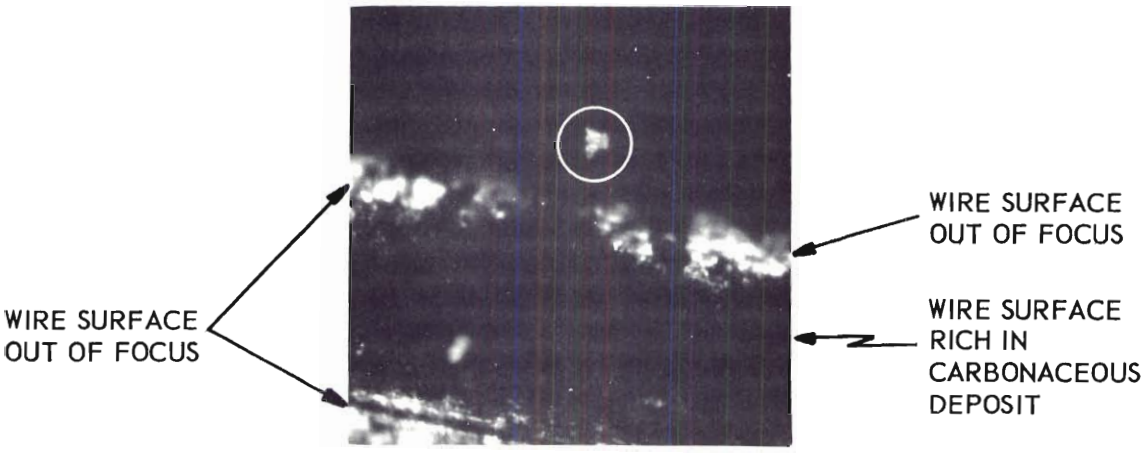


PLATE 1

Large Metal-like Particle (circle) in Carbonaceous Deposits on Surface of Wire from Run 30. Magnification: Englargement to about 200X from 10X negative. Particle protruding from side of wire as viewed in microscope for photograph.

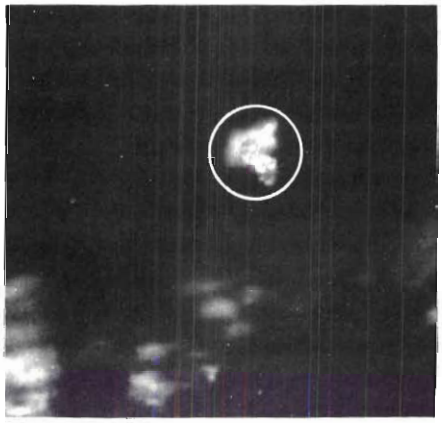


PLATE 2

Same Specimen and View as in Plate 1, above. Magnification: Enlargement to about 500X from 10X negative.

Figure 6a. Examples of Metal-like Particle in Carbonaceous Deposits on Surface of Type 304 Stainless Steel Wire.

of the wire diameter (0.01 inches) in size. Results of the counts are given in Table IX. In all the counts of Table IX, only one side of the one inch long wire specimens was observed. All particles observed were counted and one of the sizes shown in Table IX was assigned to each particle. That is, each approximate size indicated represents a narrow distribution of sizes in reality. For clarity, the accompanying description and results of Runs 12, 26, 27 and 32 are repeated in Table IX.

Metallurgical Examinations.--A number of metallurgical examinations were made. For example, specimens were examined from Runs 3, 9, 12, 17, 24 - 27, as well as "as received" wires. Only a few examinations were made on specimens from all of these runs except Runs 17 and 26. Run 26 showed the most promising results and consequently, effort was concentrated on these specimens.

Run 3 was made using nickel wire specimens. Metallurgical examination of samples of this specimen revealed little, if any, discernable changes in the wire cross-sections which were observed. Similarly, no significant changes were observed on the Inconel specimen of Run 9. It is unknown whether localized attack of either the Inconel or nickel specimens had taken place. Attacked zones in the wires were extremely difficult to find using normal metallurgical techniques. The difficulties arose, primarily, from the inherent complexities of examination of small samples with localized, and indeed small, surface changes. However, an examination of a sample of Run 17 showed promising results for the first time. Localized intergranular attack of this specimen was found. Changes in wire diameters were of immeasurable magnitude for all specimens analyzed.

Table IX

Approximate Metallic-like Particle Sizes and Counts in Carbonaceous Surface Deposits on Type 304 Steel Wires

Observed surface: 1 side of 1 inch long wire.

D = wire diameter (0.01 inch), d = approximate particle diameter.

Sample Description	Total Number of Particles		Approximate Numbers and Sizes of Particles Observed			
			$d \leq D/30$	$d \approx D/20$	$d \approx D/15$	$d \geq D/10$
As received	19		3	10	3	4
Run 32	12		6	6	--	--
Run 12	21		15	3	1	2
Run 12, tapped	5	36	1	3	1	--
Run 12, wiped	10		5	4	1	--
Run 27	44		23	14	3	4
Run 27, tapped	34	91	18	7	7	2
Run 27, wiped	13		6	4	2	1
Run 26	34		12	6	6	10
Run 26, tapped	92	226	36	14	27	15
Run 26, wiped	100		61	20	18	1

Exposure Conditions:

Run 12: 16 hours, 0.97 SCFH* CO, 1020° F., 0.15% weight gain.

Run 26: 120 hours, 0.92 SCFH* CO, 1065° F., 2.11% weight gain.

Run 27: 16 hours, 0.29 SCFH* CO, 1105° F., 1.49% weight gain.

Run 32: $17\frac{1}{4}$ hours, ca. 1 SCFH* N_2, 1065° F.

*SCFH = standard cubic feet per hour.

This, however, was not unusual, since uniform surface attack, in very severe cases, would theoretically result in a diameter decrease of about 0.1 per cent (circa 0.00001 inch). This estimate is based on a metal content of about 10 weight per cent in a heavy carbonaceous deposit. A heavy carbonaceous deposit was considered to be about 2 per cent of the wire weight. Further, the estimate does not take into account the penetration of carbon into the wires. Hence, metallurgical examinations suffered considerable limitations.

Samples were prepared by mounting the wire specimens in a cold setting epoxy resin (five parts by weight of Bakelite ERL2795 epoxy resin mixed with one part of Bakelite ZZLD0814 hardener). These mounted specimens were then ground down and polished through A. Buehler's 1557 AB Gamma Polishing Alumina Number 3 or 1554 AB Metpolish Number 3. Various specimens were observed for signs of attack on the metals. As stated earlier, definitely attacked areas were difficult to locate. However, a few cases of intergranular attack of the Type 304 stainless steel, in localized areas, were very definitely observed. Illustrations of the intergranular attack are shown in Figures 7 and 8. The pictures shown in Figure 7 were taken of a sample from Run 26 (CO exposure for 120 hours at 1065° F.), and they represent the highest degree of intergranular attack which was observed in any single cross-sectional examination. Included in Figure 7 are views of the following:

1. Specimen from Run 26 unetched.
2. Specimen from Run 26 etched.

A higher magnification of a section of the above two wire pictures is given in Figure 7a. All the above mentioned pictures were taken on the

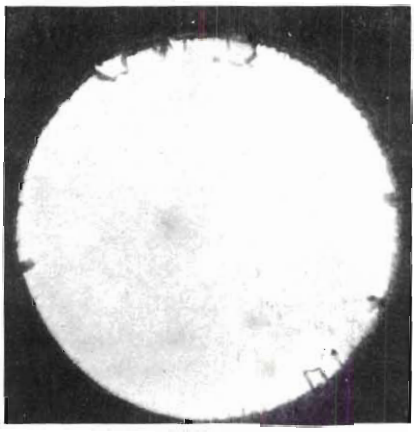


PLATE 1

Cross-sectional View of Sample from Run 26. Magnification: 200X. No Etch.

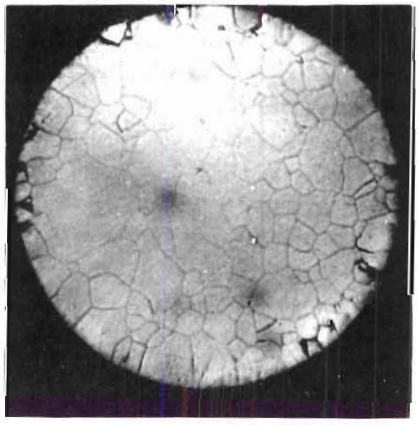


PLATE 2

Same Sample as in Plate 1, After Etching. Magnification: 200X. Etchant: 40% Marble's Reagent in Glycerin.

Figure 7. Type 304 Stainless Steel Wire Specimen Showing Intergranular Attack by Exposure to Carbon Monoxide.

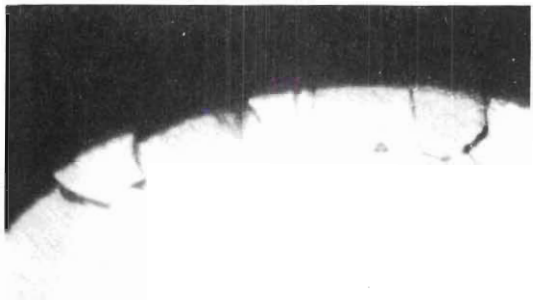


PLATE 1

Section of Sample in Figure 7, Plate 1. Magnification: 500X.

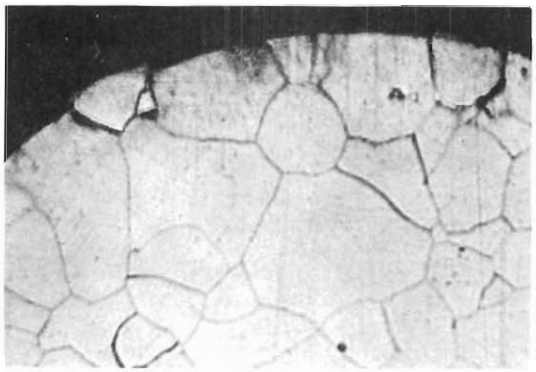


PLATE 2

Section of Sample in Figure 7, Plate 2. Magnification: 500X. Note that this is same section as in Plate 1, above, after etching specimen.

Figure 7a. Type 304 Stainless Steel Wire Specimen Showing Intergranular Attack by Exposure to Carbon Monoxide.

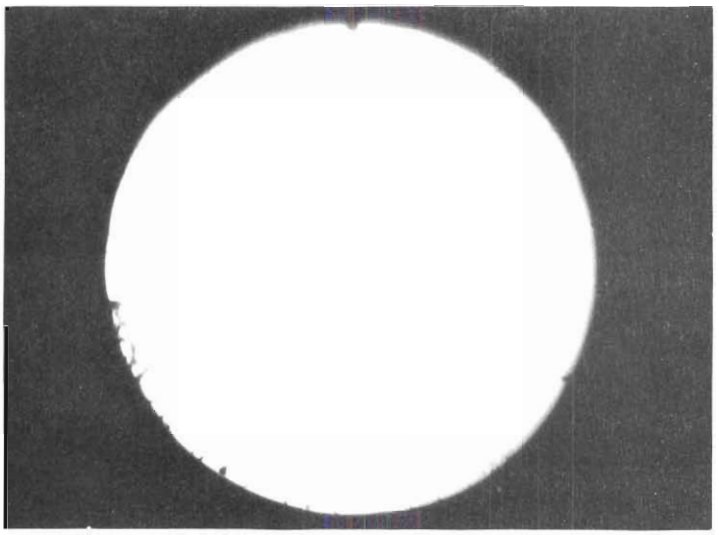


PLATE 1

Type 304 Steel Wire in Cross-section From Run 26. Magnification: 250X. Etch: None.

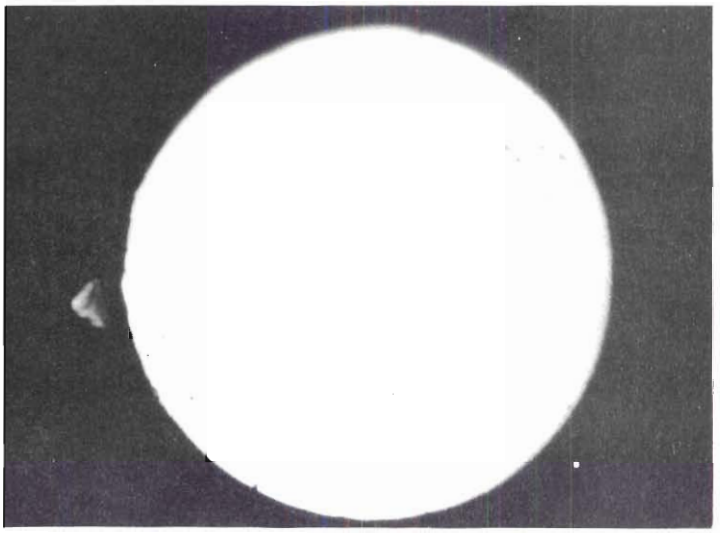


PLATE 2

Type 304 Steel Wire and Metal-like Particle Near Surface. Sample From Run 26. Magnification : 250X. Etch: None.

Figure 8. Other Examples of Effect of Carbon Monoxide on Type 304 Stainless Steel at About 1065° F.

same specimen. The unetched specimen from Run 26 clearly shows intergranular attack. The etched specimen photograph substantiates that the attack is definitely intergranular. After etching, this same sample was repolished (using only 1554 AB Metpolish Number 3) in order to prepare the sample for electron micro-probe analysis. While repolishing this sample, a few of the attacked grains were completely removed by the light polishing operation. The grain removal is shown in the photograph of the repolished specimen in Figure 9, Plate 2. For purposes of comparison, a cross-sectional view of an "as received" sample of the Type 304 stainless steel wire is also shown in Figure 9.

Electron Micro-probe Analyses.--An electron micro-probe analyzer* was used to analyze individual grains of the attacked specimen (repolished) from Run 26 which was discussed above. Also, attempts were made to analyze some of the metallic-like particles in the carbonaceous surface deposits using the electron micro-probe analyzer. Photographs of the analyzed specimen, with identification of the points of analysis, are given in Figure 10. Results of the electron micro-probe analyses are given in Table X below the photograph in Figure 10.

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*An electron micro-probe analyzer is an analytical instrument in which a beam of high energy electrons is directed onto an analytical specimen in a very small area. Electron beam width and control of beam path allow analysis of a region approximately one micron in diameter. Through absorption of some of the energy of the electron beam, inner shell electrons of the specimen material are excited. Outer shell electrons, in falling into the inner vacancies, emit characteristic X-radiation. This radiation is metered by a Geiger counter and is an indication (by spectral principles) of composition of the specimen. The electron micro-probe analyzer used in this work was made available through the courtesy of International Nickel Company, Incorporated.

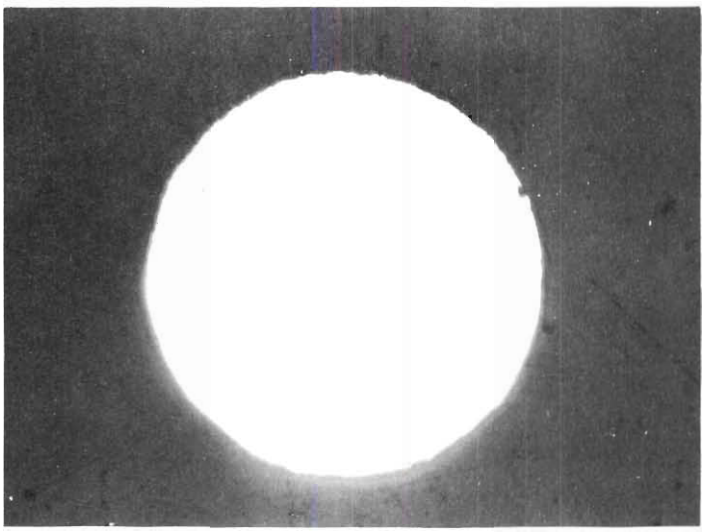


PLATE 1

Specimen of as Received Wire. Magnification: 200X. No Etch.

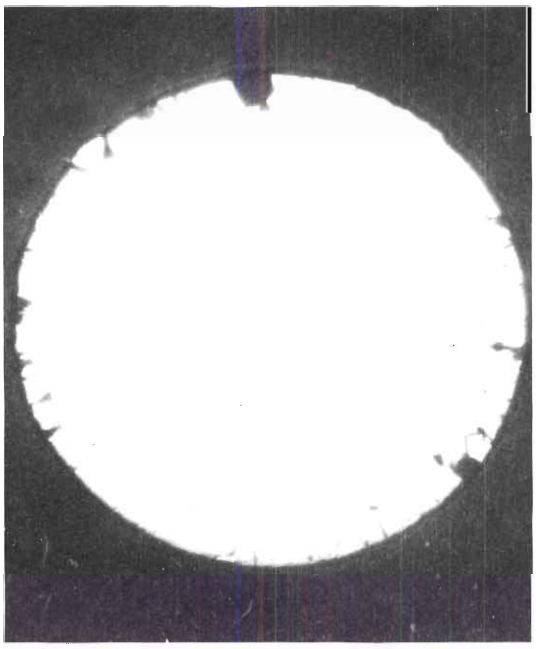
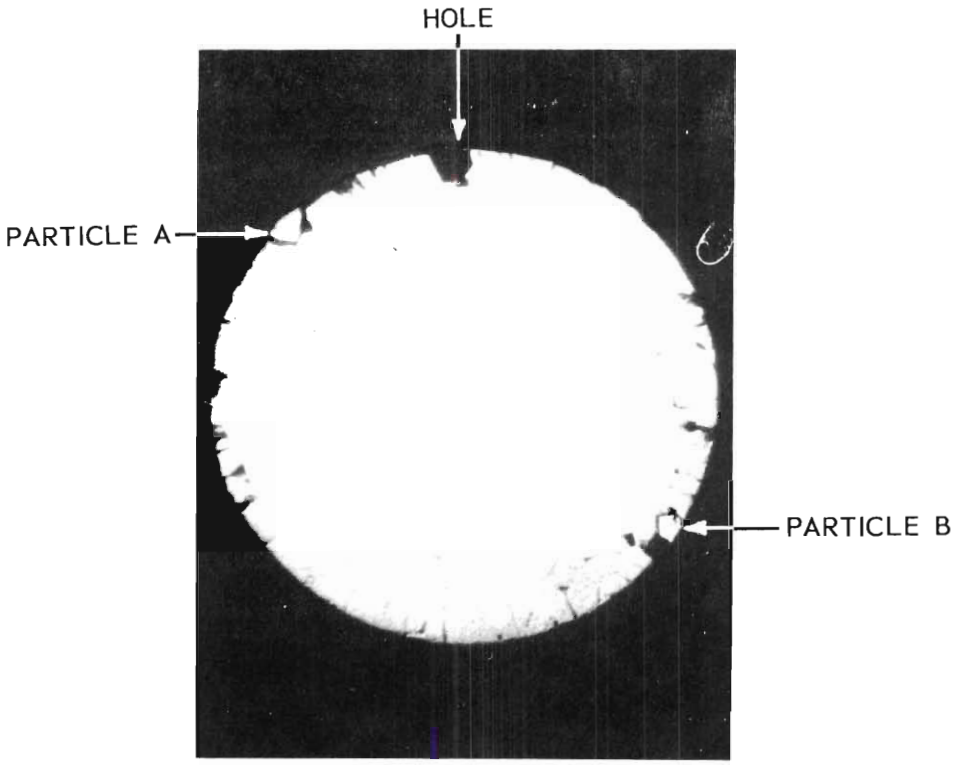


PLATE 2

Specimen: Sample from Run 26. Same Specimen as in Figure 7 after repolishing. Magnification: 250X. Note loss of grains by repolishing.

Figure 9. Cross-sectional Views of Type 304 Stainless Steel Wires.



SAMPLE FROM RUN 26 AT 250X – REFER TO PLATE 2, FIGURE 9

Figure 10. Electron Micro-probe Analyser Specimen From Run 26.

TABLE X
ELECTRON MICRO-PROBE ANALYSER RESULTS

LOCATION (REFER TO FIGURE 10)	APPROXIMATE COMPOSITION, ATOMIC PER CENT		
	Fe	Cr	Ni
Matrix, near center of wire.	66.0	23.2	7.8
Particle A, near center.	66.0	21.0	6.6
Boundary about Particle A.	20.7	20.3	2.0
Particle B, near center.	67.2	19.9	7.6
Particle B, near edge.		20.0	6.2
Hole	5.7	5.9	Nil

The sample of carbonaceous surface deposit shown in Figure 11 was prepared from material dusted from the wire sample from Run 25. This sample was slightly compressed in the shape of a hemisphere about $\frac{1}{4}$ inch in diameter and mounted in the epoxy resin. This mounting was done in much the same manner as that for the wire specimens. The mounted deposit sample was then ground down and polished through A. Buehler's 1554 Metpolish Number 3. In an attempt to analyze this sample with the electron micro-probe analyzer, the polished specimen was first coated with a very thin film of evaporated carbon. This carbon was coated on the specimen for the purpose of conducting electrical charge away from the surface on exposure to the electron beam. Particularly when the electrical conductivity of the analyzer specimens is low, the path of the electron beam cannot be controlled well. Results of the analysis of the deposit sample were not considered satisfactory. However, referring to Figure 11, the large particle (circle) was found to be high in silicon and is suspected to have been embedded there when polishing the sample with silicon carbide. A few other smaller metallic particles near the large particle, discussed above, were examined with the micro-probe analyzer. Appreciable amounts of iron and slight amounts of nickel were indicated. These particles gave no indications of having measurable chromium contents.

Tests for Sensitization of Type 304 Stainless Steel.--Tests for sensitization for intergranular attack of the Type 304 stainless steel wires were made in the following manner. One wire specimen was placed in the experimental reactor in an atmosphere of nitrogen, at 1065° F., for a

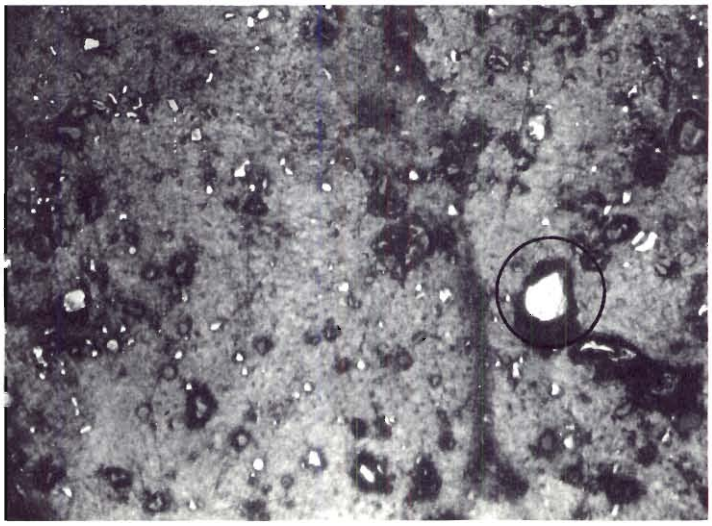


PLATE 1

Surface Deposit Specimen Mounted in Epoxy Resin. Magnification: 250X. Deposit Source: Run 25.

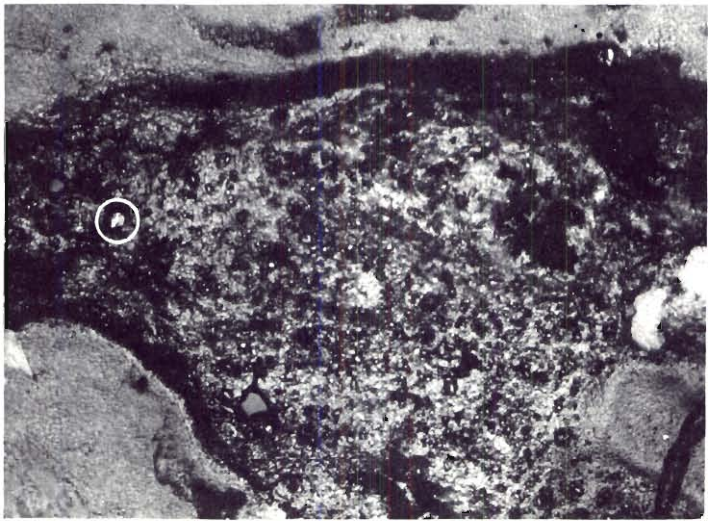


PLATE 2

Specimen of Plate 1, above, Showing Carbonaceous Material Littered With Metal-like Particles in Epoxy Resin Mounting. Magnification: 100X.

Figure 11. Carbonaceous Surface Deposit Specimen Mounted for Electron Micro-probe Analysis.

period of 8 hours. A second wire specimen was likewise heat-treated for 16 hours. Samples of each of these heat-treated and a sample of "as received" wire were placed in boiling nitric acid (concentrated) for periods of 8, 16, and 24 hours. These nine samples were each weighed before and after acid treatment. Weight loss of the specimens tended to increase with both heat-treatment time and acid treatment time. This is shown in the following tabulation, which gives weight losses as weight percentages for the various specimens. The specimen sizes ranged in weight from 1.7468 to 2.0050 grams.

Weight Losses of Type 304 Stainless Steel Wires After Heat Treatment at 1065° F. and Boiling in Nitric Acid

Hours of Heat Treat at 1065° F.	Weight Losses of Wires After Indicated Hours of Boiling in Concentrated HNO_3		
	8 hours	16 hours	24 hours
0	0.25%	0.32%	0.76%
8	0.37%	0.52%	0.87%
16	0.66%	0.51%	1.01%

The above discussed test is a modified Huey* test. Microscopic examination of cross-sections of these wires showed only surface attack, by the acid, but no intergranular attack. It was concluded that heat treatment for 16 hours at 1065° F. did not produce sensitization of the stainless steel.

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*"Boiling Nitric Acid Test for Corrosion Resisting Steels", A.S.T.M. Designation A262-55T, A.S.T.M. Standards, Part 1, Ferrous Metals, 1955, 1108-1118.

Examination of a Specimen of Inconel Used in Industrial Service.--A specimen, illustrating the long term destructive effects of gases containing carbon monoxide, was briefly studied in the presently discussed research. This specimen was a field sample in the form of a plate approximately three inches by five inches. The material was Inconel and it was 3/16 inch plate stock. The sample had about 20 pits on the side which had been exposed to gas containing carbon monoxide, hydrogen, and nitrogen as principal constituents. The pits were nearly hemispherical and varied in diameter from about 1/8 inch to 3/8 inch. Dr. E. N. Skinner, of International Nickel Company, Inc., described this plate as part of a carburizing atmosphere generator. The generator burned natural gas with controlled amounts of air. The burned gas was passed over nickel catalyst to generate carbon monoxide and hydrogen from the excess natural gas, water, and carbon dioxide. The generator was operated at temperatures near 1700° F. However, the location of attack of the Inconel generator wall was in a zone where the temperature was cooler than 1700° F., although the exact temperature of this zone was unknown. This particular part of the Inconel wall was just outside the furnace which heated the generator. Carbon deposition was observed in the attacked area of the generator. The generator had been in operation for about a year when the pitted sample was removed.

There were no loose carbonaceous deposits on the surface of the Inconel field specimen after it was removed and handled. However, a small amount of compact carbonaceous deposit remained in the hemispherical pits. For the presently discussed examination some of this deposit was

removed. The deposit was ferro-magnetic. An X-ray diffraction analysis of the deposit is given in Appendix C, Analysis 11, page 128. This diffraction pattern was very similar to diffraction patterns obtained by analysis of carbonaceous deposits on the stainless steel wire specimens of the present experimental work. Microscopic examination of the Inconel field specimen revealed that it had been attacked, intergranularly in localized areas. This attack was similar to that observed on the stainless steel wires in the presently discussed experimental work. Pitting of the specimen was apparently the result of continued localized intergranular attack of the metal by the gaseous atmosphere.

CHAPTER V

ANALYSIS OF RESULTS, CONCLUSIONS AND RECOMMENDATIONS

Discussion and Analysis of Results.--Essentially, the experimental results of this research dealt with the following:

1. Temperature dependency of carbonaceous weight gains on Type 304 stainless steel wires when exposed to carbon monoxide.

2. Effect of carbon monoxide exposure time on the amount of carbonaceous deposits of 1.

3. Analytical inspections of the stainless steel wires and surface deposits for indications of possible solid state reaction intermediates.

4. Qualitative tests for metal carbonyls in the experimentally exposed carbon monoxide.

5. Limited investigation of the effects of carbon monoxide on commercially pure nickel and Inconel wires.

In the following discussion and analysis of results, subjects which are considered are:

1. Variability of the amounts of carbonaceous weight gains on the stainless steel wires which were exposed to carbon monoxide at 920-1100° F.

2. Limitations of the indicated effects of temperature on the amounts of carbonaceous weight gains of exposed wires.

3. Comparison of amounts of carbonaceous weight gains with those obtained on similar materials in other research.

4. Mathematical determinations of activation energies of reactions producing carbonaceous surface deposits.

5. Limitations of analytical inspections of the carbonaceous surface deposits for metal components.

6. Mathematical determinations of activation energies of reactions which produce carbon in the main body of exposed stainless steel wires.

7. Comparison of activation energies of 6 with the activation energies for diffusion of carbon monoxide and carbon in some pure metals.

8. Brief discussion of the limited experimental results on Inconel and nickel.

9. Theoretical discussion of unstable reaction intermediates.

10. Inferences from experimental findings concerning the mechanism of carbon monoxide attack on Type 304 stainless steel.

Carbonaceous Weight Gains of Type 304 Stainless Steel Wires.--Upon inspection of Figure 4, page 45, one sees that the amounts of carbonaceous deposits on the wire surfaces were reasonably variable even at essentially fixed exposure conditions. Potential sources of variability in this system were temperature accuracy, gas purity, loss of deposit matter by gas entrainment, and normal non-uniformities in composition and surface characteristics of the wire specimens.

Likely, the variability of actual temperatures, compared to indicated ones, were well within the limits of $\pm$ 15°F. This is the rated accuracy of the instruments which were given by the supplier. Some test

work (refer to the description of apparatus on pages 115-116) indicated that the reactor temperature recorder-controller accuracies were well within the rated values. However, approximately two-thirds of the scatter in the data of Figure 4 is within the range equivalent to ± 15° F. Thus, temperature accuracy is surely a significant factor in variations of experimental results. A review of experimental notes revealed that data which deviated most from the graphical curve of Figure 4 were obtained with carbon monoxide containing about 0.5-0.6 volume per cent carbon dioxide. Normally, the cylinder carbon monoxide contained less than 0.2 volume per cent carbon dioxide, even after long standing. However, Runs 14 and 16 were made with carbon monoxide which had apparently decomposed more than usual. This suggested that carbon monoxide purity was also a potential source of appreciable variability. Carbon monoxide rate is a potential source of variability from the point of view of surface deposit entrainment by the gas. Four of the points in Figure 4 were obtained with carbon monoxide rates of about 0.3 standard cubic feet per hour. The other data in this graph were obtained with carbon monoxide rates near one standard cubic foot per hour. Concerning possible entrainment, it is noteworthy that three out of four of the points with lower gas rates are above the curve.

In attempts to quantify the variability in Figure 4, an approximate statistical error analysis was made. This analysis was based on deviations of measured weight gains from the graphical curve values. For the analysis, deviations (individual weight gains minus the curve values) were taken from Figure 4. These deviations were converted into percentages of the weight gains given by the curve. These percentages

were treated as normal or Gaussian error statistics. Results of this analysis were: -9 per cent average deviation from the curve with a standard error of 43 per cent. Although less variability was desirable, the amount indicated is reasonable, since a catalytic process is involved.

In order to represent the data of Figure 4 analytically, an Arrhenius relationship (rate proportional to exponential -b/T) between weight gains and temperature was assumed. Only data which were obtained with a carbon monoxide rate near one standard cubic foot per hour and a carbon dioxide content of less than 0.3 volume per cent were used. Thus, data from Runs 12, 13, 18, 19, 20, 21, 25, 27, 29, 30, and 31 were used in these calculations. All of these experiments were made with sixteen hours exposure times. Weight gains, w, were assumed to be theoretically expressed as:

$$w = ae^{-b/T} \qquad (1)$$

where, w = weight gain in 16 hours exposure, weight per cent.

a = a constant.

e = base of the natural logarithm.

b = activation energy of the reaction/gas constant, °R.

T = absolute reaction temperature, °R.

Obtaining natural logarithms (denoted by ln) of both sides of equation (1), one has,

$$\ln w = \ln a - b/T \qquad (2).$$

A least squares fit of the data to equation (2) was obtained and the results were:

$$\ln a = 25.7322$$

$$b = 40,151 \text{ degrees Rankine.}$$

The estimated standard deviation of b was $\pm$ 5,835 degrees Rankine. Thus, the estimated value of b for the surface deposit reaction ($\pm$ 2 standard deviations) was taken as approximately 40,150 ($\pm$ 11,500) degrees. This is equivalent to an activation energy of about 44,300 ($\pm$ 12,850) calories per mole.

Experimental results indicated that rates of carbonaceous weight gains tended to decrease when exposure periods were from 16 to 120 hours. For example, carbonaceous weight gains in Runs 24 and 26 were both near 2.1 per cent. These runs were made at 1065° F. However, the exposure times for these two runs were 32 and 120 hours, respectively. Even in view of system variability, it must be concluded that reactivity tends to decrease with time. The weight gain of Run 24 does appear high in comparison to the average value for 16 hour runs at 1065° F. For example, Figure 4 indicates a weight gain of about 0.56 weight per cent at 1065° F. for 16 hours exposure. Since the weight gain for Run 24, above, is indicated to be more than twice this value, one might suspect that reactivity increased between 16 and 32 hours exposure. However, this is considered to be due to experimental error and not necessarily a real effect. Further, enough experiments at 32 hours exposure times to prepare a graph similar to Figure 4 was considered unjustified to resolve this question at the expense of other problems of more concern. The

point is that reactivity is indicated to decrease with time. Decrease of activity with time is not entirely surprizing. One needs only to consider the fact that deposition is taking place. Further, others have experienced similar findings. For example, Baukloh and Heiber (13) obtained weight gains of carbon (according to these research workers) on powdered iron upon exposure to carbon monoxide. These weight gains were orders of magnitudes greater than those found in the present experimental work. For example, calculations indicated that Baukloh and Heiber obtained weight gains of the order of 10 to 40 grams/hour/foot^2 when iron powder was exposed to carbon monoxide at about 1065° F. for 30 minutes. This deposition flux cannot be compared directly with the results on the stainless steel wires. Obviously, direct comparison is limited by differences in the composition and physical structure of the metal specimens, exposure times and other experimental factors. However, Table VI, page 49, shows that weight gains were about 0.0168 grams/hour/foot^2 when the stainless steel wires were exposed to carbon monoxide for 16 hours at 1065° F., in the present experimental work. Baukloh and Heiber do, however, indicate that there was an optimum exposure time with respect to deposition rate. Their data indicated an increase in deposition rate with time up to about 4 hours exposure. After about four hours, the deposition rates decreased.

Figure 4 shows a steady increase in weight with increasing temperature, at constant exposure time. It is believed likely, however, in view of the results of Baukloh and others, that a maximum weight gain would have been found at still higher temperatures. For example, Baukloh

and Heiber (13) concluded that approximately 550° C. was optimum for weight gains of iron and iron oxide powders when subjected to carbon monoxide. Berry, Ames and Snow (12) showed similar results on ferric oxide powders which were exposed to carbon monoxide and carbon monoxide-hydrogen mixtures. The maximum weight gains indicated by these investigators occurred between about 900 and 1200° F. They showed essentially no deposition below about 700° F. and above about 1300° F. The Babcock and Wilcox Company data given in Table IV, page 28, was analyzed for temperatures of maximum weight losses of some of the 300 and 400 series stainless steels. In the analysis, the percentage weight losses were expressed as a third degree polynomial in temperature by methods of least squares curve fitting. These polynomials were differentiated and the temperatures of maximum weight loss were estimated. Typically, the critical temperatures were in the range of 1160 to 1270° F. In particular, the critical temperature for Type 304 stainless steel was estimated to be about 1190° F. The relationship of the weight loss experience of Babcock and Wilcox to the weight gains under present study is uncertain. However, the results of the study of the Babcock and Wilcox information is presented in further support to the proposal of critical, or extremum, temperatures in the range of 1000 to 1300° F.

Inspections of Wire Specimens and Surface Deposits.--Figure 7, Plate 1 clearly shows that intergranular attack of the wire specimens took place on exposure of the stainless steel to carbon monoxide. Several analytical techniques were used in attempts to determine the products of the attack and/or the composition of the intergranular material. These analytical

methods included (a) chemical and X-ray fluorescence analysis of the surface deposits, (b) X-ray diffraction analysis of the surface deposits and wire specimens, (c) electron micro-probe analysis of individual grains of the wire shown in Figure 7 and (d) chemical analysis of various wire specimens for carbon penetration. Some rather interesting information was accumulated from the analytical efforts. However, no entirely satisfactory conclusions were reached as to the chemical species involved in the metal attack process.

One conclusion reached was that physical separation of the components in the surface deposits might be practical in connection with X-ray diffraction analysis. However, even with very efficient separation methods, physical separation of the small amounts of material obtained in this experimental work was considered impractical. For example, if relatively high quantities (about 75%) of the metal components were separated from the entire surface deposit of Run 26, the amount of total metal containing components would only be chemically equivalent to about 14 milligrams of iron and 2 milligrams of nickel. Here, it should be recalled that Run 26 was made at 1065° F. with an exposure time of 120 hours, and yielded about a maximum carbon deposit.

Since the X-ray diffraction analyses were inconclusive in identifying structures of the products of the carbon monoxide attack reaction, other less specific information was sought out. It was felt that much of the intergranular material indicated in Figure 7, Plate 1 was carbon or carbonaceous. Hence, the carbon penetration analyses, which are shown in Table VII, page 51, were made. These

carbon analyses, on the cleaned wire specimens from Runs 12, 20, 26 and 27, were conclusive in demonstrating that carbonaceous penetration had taken place. A mathematical analysis was made on the carbon content data from Runs 12, 20, and 27. These three runs were all made with 16 hours exposure time and at temperatures of 1020, 920, and 1105° F., respectively. In the same order, the cleaned wire carbon contents were 0.14, 0.08, and 0.63 weight per cent, respectively. The analysis was similar to that discussed on pages 79 and 80 dealing with exposed wire weight gains. Values for the mathematical analysis on carbon content increases were obtained from the above three carbon contents less 0.05. That is, the carbon content of the untreated stainless steel wires were subtracted from each of the exposed wire values for mathematical treatment. Since this analysis was based on data from only three runs, the results must be considered cautiously. Nevertheless, the activation energy for the reaction which produced carbon in the interior of the wires was estimated to be about 37,300 calories/mole. This value is nearly the same as that calculated for weight gains (including surface deposition) on page 80. Further, when one considers the variability of the data, the activation energies for the two processes cannot be considered different from one another. Limited information from technical literature shows that the activation energies for rates of diffusion of carbon in nickel, steel and α iron are in the range of those calculated above. For example, Smithals and Ransley (27) reported on the diffusivities of carbon and carbon monoxide in nickel, and carbon in steel. These diffusivities were based on measurements

made at much higher temperatures (1652-2012° F.) than those of concern in the present experimental work. However, calculations based on the information of Smithals and Ransley gave the following activation energies.

System	Activation Energy, calories/mole.
Carbon in nickel	41,000
Carbon monoxide in nickel	40,100
Carbon in steel	49,600

These authors reported that the carbon monoxide measurements were confused by decomposition of the carbon monoxide in the nickel resulting in carbon formation. Wert (28) gave the activation energy for the diffusion of carbon in α iron for the temperature range of -40 to 800° C. This value was 20,100 calories/mole. Wells and Mehl (29, 30) gave some interesting information concerning the effects of nickel on the diffusion rate of carbon in steel at 1000° C. For example, they stated that up to about 2 per cent nickel, the effect on diffusion was negligible. On the other hand, at 3 atomic per cent carbon, the diffusivity of carbon in austenite at 1000° C. is increased from about 3.6×10^{-7} centimeters/second in a plain carbon steel to 4.6×10^{-7} centimeters/second in a 20 per cent nickel steel. These authors give various other information on the effects of composition on diffusion rates of nickel in iron and carbon in steel. However, this information is rather involved for presentation here, and only reference will be made to this work. In view of the activation energy calculations,

above, and the following discussion, it was concluded that a carbon or carbon monoxide diffusion controlled process was entirely possible for the reaction of carbon monoxide with the stainless steel wires.

As stated earlier, X-ray diffraction analysis was considered inconclusive in identifying chemical structures of the carbonaceous surface deposits. However, referring to Appendix C, page 127, Analysis Numbers 10 and 11, the resemblance of the diffraction pattern for the Inconel field sample deposits and that of the wire surface deposits is striking. This suggests that the field corrosion process must be similar to those involved in the present experimental work.

Referring to Table IX, page 63, on counts of particles such as illustrated in Figure 6, page 60, one sees that the quantity of metallic-like particles in the carbonaceous surface deposits is quite appreciable. The particle counts have many limitations, and they were considered not amenable to critical calculation. However, if one assumes a particle size distribution similar to those indicated for Run 26, an average particle size of about 0.0007 inch is obtained. This value is based on the average cubed diameter. Chemical analysis showed that the surface deposit of Run 26 contained about 7.5 weight per cent iron and 1 weight per cent nickel. If one assumes that the metal in the surface deposit was comprised of pure metal spheres, with an average diameter of 0.0007 inch, then about 700-800 spheres per inch of wire would be required for the indicated chemical composition. Referring to the particle counts on page 63 (Table IX), the number of metallic-like particles per inch of wire for Run 26 was shown to be of the order of a few hundred. The manner in which the counts were made

tended to make the counts lower than the actual number of particles present. This was due to masking of the metallic-like particles by carbon. In view of these facts, a considerable, but indefinite, amount of the metal contents of the surface deposits were suggested to be in the metallic-like particles which were counted.

In connection with the experiments in which tests for carbonyls were made, one item of particular concern was the amount of cold trap condensate. This condensate surely came into the gas stream in, or after, the reactor. This can be said, for a similar cold trap was in the carbon monoxide stream prior to the reactor. There was a very small amount of condensate in the trap before the reactor, but it completely vaporized even before the trap warmed to room temperature. Thus, the cold trap condensate in the effluent steam was concluded to have originated in, or after, the reactor. On the basis that the condensate in the trap after the reactor was water, it was estimated to be about 0.1 volume per cent of the exposed carbon monoxide. This is equivalent to a dew point of about -20° C.

Data on Commercially Pure Nickel and Inconel.--Several inspections of the Inconel and nickel wire specimens were made. These included X-ray diffraction, microscopic and metallurgical examination. No significant changes in these exposed materials were observed. It was concluded that if definite attack of the materials by carbon monoxide were to be demonstrated, severity of exposure conditions must be increased. In addition, by comparison of results with those for stainless steel, as shown on page 49, one may conclude that the stainless steel was

about one order of magnitude more reactive than nickel and Inconel. In this sense, carbon monoxide exposure times of about 1000-3000 hours near 1100° F. could be considered reasonable for testing nickel and Inconel for measurable attack. Such extensive exposure times were beyond the scope of the present research program.

Surface deposits on the nickel and Inconel specimens were insufficient in quantity to analyze. However, in the most severe cases (16 hours at 1100° F.), an extremely small amount of deposit was dusted from the surface of both the nickel and Inconel specimens. This carbonaceous dust could be lifted with a magnet. Although the dust was slightly magnetic, it did not appear to be as sensitive to the magnet at the dust from the stainless steel.

Theoretical Discussion of Experimental Results.--The results of this research work has been inconclusive in defining the chemical processes involved in the carbon monoxide attack on Type 304 stainless steel. However, a composite analysis of the entire set of exploratory results tends to indicate that unstable reaction intermediates were formed. Clearly, the composition of the metal components in the surface deposits on the stainless steel was drastically different from the initial wire composition, especially since chromium was almost completely absent. This evidence almost excludes the possibility that metal was mechanically forced from the base metal by carbon deposition. On the other hand, the surface deposits contained a small amount of chromium. Therefore, a small amount of mechanical removal of metal grains by carbon deposition cannot be entirely ruled out of the metal transfer process. However, a

low degree of mechanical removal of metal is certainly indicated. The X-ray diffraction analyses, although indefinite, most strongly favor metal or alloy-like structures for the metal components in the surface deposits as contrasted to carbides. In view of all these facts, unstable reaction intermediates are almost certain.

Considering the system dealt with here, one surely recognizes the carbides and carbonyls as potential unstable intermediate species. Referring to Chapter II, it is evident that all well known carbides and carbonyls of iron and nickel are thermodynamically unstable at temperatures in the range of concern. Further, it is extremely doubtful that the carbides or carbonyls of iron or nickel will form at all near 1000° F. However, if they were formed, rapid decomposition would be expected. These things are the requisites for unstable intermediates, and hence, these species should be considered. The effect of alloying on the thermochemical properties of Type 304 stainless steel is unknown. Likely, the alloys of iron, nickel and chromium, such as Type 304 stainless steel, deviate considerably from ideal solid solutions. This is supported by the fact that moderate additions of nickel change the normal body centered cubic lattice structure of iron to a face centered cubic structure. Thermochemical properties of alloys of this type are not well defined. Non-ideality of the system Fe-Cr-C is clearly indicated by Kubaschewski and Catterall (31). However, these properties are given for temperatures very much higher than those of concern in the present case. The activity of grain boundary regions, from the thermodynamic point of view, of normal Type 304 stainless steel is

also very ill defined. Possibly, due to defects and the like, increased reactivity of grain boundary regions may best account for the formation of unstable reaction intermediates with carbon monoxide. This seems most likely of the two things considered above, since it is well established that cast iron (as contrasted with alloys) is reactive with carbon monoxide in a similar manner to Type 304 stainless steel.

Inferences from Experimental Results Concerning the Attack of Type 304 Stainless Steel by Carbon Monoxide Near 1000° F.--Clearly, one cannot say that the experimental findings of this research defines the mechanism of the attack of Type 304 stainless steel by carbon monoxide. On the other hand, several pertinent exploratory results have come from this work on Type 304 stainless steel. By way of review, these include:

(a) Type 304 stainless steel wires were attacked by high purity carbon monoxide at temperatures between 920 and 1100° F.

(b) Coincidental, or incidental, with the attack of carbon monoxide on the stainless steel, appreciable amounts of graphitic carbon was formed, especially at temperatures higher than about 1020° F. This carbon tended to accumulate in magnetic surface deposits (Type 304 steel is non-magnetic) on the stainless steel wires, but a measurable amount of carbon was shown to have penetrated into the main body of the wires.

(c) For 16 hours exposure of Type 304 stainless steel to carbon monoxide, the amount of surface deposition, as

indicated by weight increases, increased with temperature in the range of 920 to 1100° F.

(d) Microscopic examination of the surface deposits on the wires showed that the carbonaceous deposits contained appreciable numbers of metallic-like particles. These particles varied in size, but were indicated to average about 0.0005 to 0.0007 inch in diameter. This size was based on some qualitative particle counts. Further, it is pertinent to state here that, coincidentally or otherwise, the metal grains of the wires was about this same size.*

(e) Metallurgical examination of exposed wire specimens of Type 304 stainless steel showed that the wires had been intergranularly attacked, at least in localized areas. These examinations indicated some possible mechanical removal of individual grains of the stainless steel by carbonaceous deposition in the attacked grain boundaries.

(f) Chemical analysis of the carbonaceous surface deposits showed that they contained appreciable amounts of iron (about 7 - 12%), some nickel (about 1 - 4%), and very little chromium (near 0.3% or less). Thus the Ni/Cr ratio is very different from that of the parent 304 steel.

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*For example, the etched wire specimen in Figure 7, Plate 2, page 65 shows about 170 grains. Thus, the average grain size is approximately 0.0008 inch.

(g) X-ray fluorescence analyses of the carbonaceous surface deposits tended to support qualitatively the chemical analyses and indicated high iron, medium nickel and low chromium contents. Further, X-ray fluorescence analysis, of exposed wire specimens, indicated that the chromium content of the exposed wires was somewhat higher than "as received" wires. Thus, low chromium contents of the carbonaceous deposits were indicated to be compatible with the exposed wire compositions.

(h) Electron micro-probe analysis of individual grains of metal in a wire sample, showing intergranular attack and indicating mechanical removal of the grains by grain boundary deposition, showed that the composition of the grains, in the process of mechanical removal, was nearly the same as the original wire composition.

(i) X-ray diffraction analysis was inconclusive in defining the chemical species containing the metals in the carbonaceous surface deposits. However, in some of the more promising cases, X-ray diffraction suggested that the carbonaceous deposits contained graphitic carbon, nickel and iron or iron-nickel alloy-like materials. These analyses did not exclude the possibilities of small amounts of metal carbides or alloys similar to Type 304 stainless steel.

In view of the above exploratory evidence, the mechanism of carbon monoxide attack on the Type 304 stainless steel wires is suggested

to have involved formation of an unstable, metal containing, gas phase intermediate. In localized areas, the attack was indicated to be especially high along grain boundaries of the wires. Removal of metal by mechanical forces, due to carbonaceous deposition in grain boundary regions, could not be excluded, but this was indicated to be of small extent during the experimental exposure times involved.

Important arguments leading to the above suggested mechanism involve:

(a) Low chromium (relative to iron and nickel) contents of the carbonaceous surface deposits.

(b) Relatively high chromium contents of individual metal grains of the wires which were indicated nearing the stage of removal by mechanical forces due to intergranular carbonaceous deposition.

(c) Improbability of extensive migration of chromium from the metal grains in such short times and low temperatures, to give surface deposit metal high in Fe and Ni by mechanical removal of metal grains.

(d) Improbability of migration and decomposition of solid phases, such as carbides, to the extent of distributing large (circa 0.0007 inch) metallic particles in the carbonaceous deposits.

Since experimental results suggested that the reactivity of the Type 304 stainless steel wires decreased with time, likely, more severe attack of the wires would take place under alternating oxidation-carbon monoxide exposures.

Conclusions.--From this research work it was concluded that:

(1) AISI Type 304 stainless steel wires were deleteriously affected by carbon monoxide at temperatures between 920 and 1100° F.

(2) For carbon monoxide exposure times of 16 hours, the effects on the stainless steel wires increased with temperature, especially above about 1020° F.

(3) Appreciable carbonaceous deposits (up to about two per cent) were formed on the stainless steel wires upon exposure to carbon monoxide. These deposits contained measurable quantities of iron (ca. 7 - 12 per cent) and nickel (ca. 1 - 4 per cent), and small amount of chromium. The metal components of the carbonaceous deposits appeared to have resulted from decomposition of an unstable, metal containing, gas phase intermediate reaction product or products. Reaction of the carbon monoxide with the wires was indicated to be especially pronounced along metal grain boundaries, in localized areas. Possible loss of metal from the wires by mechanical forces, due to continued deposition in the affected grain boundary regions, was suggested. This possibility of mechanical metal wastage was indicated to require more severe exposure conditions to reach appreciable significance. However, loosening of grains observed in Figure 9, Plate 2, indicates that mechanical removal probably does account for some of the

grains in the surface deposits. The experimental results suggesting formation of an unstable, gas phase, intermediate was inconclusive and did not exclude the possibility of formation of an unstable, solid phase, intermediate.

(4) Limited results on commercially pure nickel and Inconel wires indicated them to be about an order of magnitude less reactive than Type 304 stainless steel with carbon monoxide, for the exposure conditions employed. Although the reactivities of nickel and Inconel were both low, the Inconel wires were indicated to be slightly more reactive than nickel wires.

(5) X-ray diffraction analysis of a carbonaceous deposit from a pitted specimen of Inconel, exposed to gases containing carbon monoxide in industrial service, showed that the deposit was very similar to the deposits formed on the experimental stainless steel wire specimens. This suggested that the corrosion processes, involved industrially, were similar to the processes studied in this research work. Since the carbonaceous deposits on this Inconel specimen were ferro-magnetic and Inconel is not ferro-magnetic, the long term corrosion process is suggested not to be the result of mechanical removal of metal by carbon deposition.

Recommendations for Further Research.--Three recommendations for further research are directed towards the following objectives.

1. Possible identification of gas phase, unstable intermediate reaction products.
2. Possible identification of solid phase, unstable intermediate reaction products.
3. Possible demonstration of mechanical metal wastage due to carbonaceous depositions in grain boundary regions.

Of course, all the above items are concerned with reaction of carbon monoxide and metals containing iron and nickel at temperatures of about 1000-1100° F., or higher.

Powdered metal specimens may show promise in the case of item 1. Undeveloped analytical techniques, unacquired chemical knowledge, and equipment costs may force this recommendation to be beyond the scope of an individual effort, such as a doctoral thesis program. However, a powdered metal reaction, potentially, could be monitored with analytical equipment such as an infra-red spectroscope. For example, the Texas Company* has explored gas-solid reaction and adsorption systems at temperatures up to 540° C. using infra-red techniques. However, metal particle sizes were quite small (of the order of 100 Å). Reference is made, in this article, to experimental work on chemi-sorbed CO on nickel and other interesting systems.

Powdered metal specimens may also be promising in the case of item 2. Reactivities of the powders should allow collection of adequate

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*Eischens, R. P., Beacon Laboratories, The Texas Company, "Infra-red Spectra of Chemisorbed Molecules". Reprint from Zeitschrift für Elektrochemie · Berichte der Bunsengellschaft für physikalische Chemie 60, Part 8, (1956), 782-788.

reaction products to attempt physical separation of the metallic components. Addition of other gases, such as hydrogen, to the carbon monoxide may also be useful in this connection. If separation and concentration of the metallic components can be successfully accomplished, conclusive structure analysis, such as from X-ray diffraction, may be possible. Further, components, such as carbides, which may be present in trace quantities, may be identified.

Recommendations for item 3 involve massive metal specimens, such as wires or sheets. Increased severity (more time and possibly higher reaction temperatures and/or pressures) will likely be required to show marked metal wastage by carbonaceous deposition in metal grain boundary regions. The experimental results on the stainless steel wires indicated that most severe temperatures were greater than 1100° F. Due to this, experimental apparatus using fluidized solids for temperature control may not be best for extended exposure times. Direct heating by high temperature resistance wires appears more suitable for this purpose, even though reaction temperature control and uniformity will be sacrificed somewhat.

If further research is done on Type 304 stainless steel wires, designed experiments should prove of value. These designs could take advantage of the exploratory findings of the present research concerning variability, effects of temperature, and exposure time.

APPENDIX A

DETAILED DESCRIPTION OF EXPERIMENTAL EQUIPMENT AND PROCEDURE

Design Basis.--Somewhat arbitrarily the experimental equipment, illustrated schematically in Figure 3, page 37, was sized on the basis of: 1. metal sample sizes of 10-50 grams, 2. carbon monoxide rates of 0.5-2 standard cubic feet per hour, and 3. reaction temperatures of 900-1100° F. This basis, except for temperature, was arbitrary. Nevertheless, the basis appeared reasonable for producing data of an experimental nature. That is, the sizes seemed to be sufficient to produce samples large enough for analysis and, yet, not be so large that materials would be wasted. The temperatures to be investigated were specified on the basis of corrosion observed in practice.

The purpose of this research work was to study the effects of carbon monoxide containing gases on nickel bearing materials at temperatures in the vicinity of 1000 degrees Fahrenheit. Thus, the design problem essentially became one of planning a system in which metal samples could be subjected to carbon monoxide containing atmospheres at these elevated temperatures under controlled conditions. At the outset of this study, information on the effects of variables was rather vague. However, whatever the design basis was to be, it appeared that rather rigid control of reaction temperature, reaction gas composition, and gas rates should be emphasized.

Description of Equipment.--The Matheson Company, Incorporated, markets compressed carbon monoxide in cylinders of about 100 cubic feet capacity.

This gas is available in a chemically pure grade which has a minimum purity of 99.5 per cent. Cylinders of this gas are used to supply the carbon monoxide in the experimentation.

For metering small gas flows, such as those involved here, commercial rotameters have been found to function well. This type meter was selected for metering the experimental gas. Two rotameters were purchased for this purpose with the following operating specifications:

Operating temperature - atmospheric.

Operating pressure - up to 150 pounds per square inch gauge.

Maximum flow rate - about 2 standard cubic feet per hour when metering carbon monoxide at atmospheric temperature and 150 pounds per square inch gauge pressure.

The meters were purchased from the Brooks Rotameter Company and were type number 1110.

It is well known that carbon monoxide, when stored for long times in steel cylinders, forms iron carbonyls. These carbonyls are of low volatility and hence the concentrations of the carbonyls in the effluent stream are low. However, removal of even small quantities of these materials from the experimental gas was desired. The carbonyls of iron are thermally unstable above about 660° F. This fact was the basis for selecting a thermal purification system which is called the CO pretreater. The pretreater consists of a coil of one half inch (outside diameter by 14 gauge wall thickness) AISI Type 446 stainless steel tubing of about sixteen linear feet. This tube is packed with clean sand. The sand provides relatively large surface for the deposition of the iron from

the carbonyl decomposition reaction. The coil, when operating, is maintained at a controlled temperature of about 700° F. by means of an electrical resistance heater. This heater is coupled with a temperature recorder controller and a chromel-alumel thermocouple. The thermocouple is located at the coil outlet.

Selection of the type of heating devices to be used in this system was rather straightforward. Electrical resistance heating was considered the most practical for the service required in this work. However, there were at least two practical ways to use electrical heating elements. The first was to simply surround the reaction zone with the elements. Second, the heating could be accomplished by means of a heat transfer medium between the heating elements and the reactor. The second type system was selected. The reactor heating system is comprised of an eighteen inch diameter vessel about three feet tall, with suitable facilities to accommodate operation as a fluidized solids temperature bath. The bath vessel is made of one-quarter inch thick plain carbon steel. Carbon steel construction was satisfactory at these temperatures since the pressures involved were nearly atmospheric. The vessel size was fixed by the space requirements of heating elements, gas preheating coils, and reactors. The original design on this bath was for three independent reactors. Only one reactor was installed, but space was allowed for three for future expansion. Auxiliaries, such as the fluidization gas supply system and the cyclone separator, are rather standard equipment for fluidized solids systems and will not be discussed here. Basically, the advantages of the fluidized solids heating system, over some of the other

systems, are that temperature control and uniformity of temperature, in relatively large zones, are usually better. The essential disadvantages are that the physical size of the fluidized solids heating system is usually larger and it is more complicated in that gas supply and solid recovery systems are required. The selection here favored temperature control and uniformity, since temperature appeared to be a critical variable in the processes under study. The bath, as it was installed, provides a fluidized bed of about eighteen inches diameter by two feet deep which is rather uniform throughout in temperature.

Preheat of the experimental gases, prior to entering the reaction zone, was desired. Therefore, a preheating coil was installed in the fluidized bed and was designed to heat the gas to within about 20° F. of the reaction temperature. It consists of about fourteen linear feet of one-quarter inch (outside diameter by 20 gauge wall) AISI Type 446 stainless steel tubing. This tubing was coiled on a four inch pipe mandril.

From the proposed experimental metal sample size and gas rate, a reactor diameter of one-half inch (outside diameter by 14 gauge wall thickness) was selected. In order to facilitate easy removal of the reactor from the fluidized bed, various auxiliary equipment such as packing glands, cocks, etc., were installed. To insure reaction in a uniform temperature zone, the metallic specimen is supported in a position in the reactor which is entirely in contact with the fluidized solids. The reactor is about five feet long and is made of AISI Type 446 stainless steel. Approximately two feet of length is potential reaction zone since this length is surrounded by fluidized solids.

Experimental product gas is hot and potentially contains entrained solid material such as carbon or metal. In order to cool the reacted gas, a coil with a water jacket was provided. This coil is about sixteen linear feet of one-quarter inch (outside diameter by 20 gauge wall thickness) AISI Type 446 stainless steel. To collect any entrained solid material, a dust settler was installed in the reaction gas exhaust line. This settler is made of five inch diameter plexiglass and is about twelve inches long. It is equipped with suitable flanges for easy dismantling and a baffle plate to insure good distribution of the gas passing through it.

It had been known for quite some time that nickel and iron are catalytically active for the decomposition of carbon monoxide according to the equation $2CO = CO_2 + C$. Thus, the experimental product gas was expected to contain both CO and CO_2. A measure of the reactivity of the metallic sample in the reactor was therefore possible through determination of the CO_2 content in the reacted gas. Sampling facilities and Orsat analytical equipment were provided for this purpose, as a control measure. To allow further analytical determinations on the reacted gas, a sampling bomb was installed. This bomb consists of twelve inches of one-half inch (outside diameter by 14 gauge wall) AISI Type 446 stainless steel tubing with valves on each end. These valves are made of Hastelloy B. The bomb is suitable for collecting samples at pressures up to about fifty pounds per square inch gauge pressure.

Since the experimental gases contain rather large amounts of CO, a vent system for safe disposal of the gas was installed. This vent consists

of four inch diameter pipe which extends about fourteen feet above the top of the building that houses the experimental equipment.

Temperature control in both the CO pretreater and in the reactor is accomplished with chromel-alumel thermocouples linked with temperature controllers. The thermocouple for the CO pretreater is fixed to the outlet of the coil with wire. The thermocouple for the reactor control is housed in a thermowell which extends to the wall of the reactor about twelve inches above the fluidized bed gas distributor plate. The gas distributor plate is at the bottom of the fluidized bed. The temperature controllers for both preheater and reactor are Leeds and Northrup Company type Speedomax H recorder-controllers. They have a range of 0 to 1500° F. The rated accuracy of this equipment is $\pm$ 15° F, although calibrations made during the course of this experimental work indicate better than this. These calibrations showed that the temperature controller would be within about 8° F. of true temperatures for about 95% of time. For a discussion on this, refer to pages 115 and 116.

To provide a means of checking the carbon monoxide feed gas purity, a sampling system was installed. This consists of necessary piping, a water cooler and a cold trap. The cold trap is for the purpose of condensing out any iron carbonyls in the pretreater effluent gas. The carbonyls of iron are liquid or solid at dry ice-acetone bath temperatures.

Materials of Construction.--Choice of construction materials which contact hot carbon monoxide containing gases in this apparatus presented quite a problem. To a large extent, this was due to the fact that the usual materials used for the temperature service required here typically

contain nickel. Since nickel bearing materials were to be subjected to the CO containing gases for study, a dilemma arose. Glass equipment was considered for construction materials in the hot regions coming in contact with the reactive gas. However, in view of its rather poor mechanical strength at elevated temperatures, and also because of the safety aspects of handling poisonous CO at moderate pressures, glass construction was rejected. Various industrial suppliers were confronted with these problems. Recommendations appeared so contradictory that no entirely satisfactory conclusions could be drawn. A technical report of the Phillips Petroleum Company (20) was available. This report contained limited information on materials durability at service conditions approximating those desired for experimentation. This company had experienced some rather severe corrosion problems and had made some laboratory tests on various materials of construction. Details of these studies are given in a paper presented at the 1959 Annual Conference of the National Association of Corrosion Engineers (25). One of the conclusions reached by Phillips Petroleum Company was that steels containing more than 25 per cent chromium appear to be fairly resistant to this type of corrosion. This information, and the desire to use materials containing no nickel (for less confusion in interpretation of experimental results), led to the selection of AISI Type 446 stainless steel for use in the reactive zones. AISI Type 446 steel has a nominal composition of 23 to 27 per cent chromium, 0.35 per cent carbon maximum, and the balance iron, except for minor impurities.

The entire reaction gas handling system from the CO pretreater to the vent was made from AISI Type 446 stainless steel except for valves.

The valves on the reacted gas sample bomb are made of Hastelloy B. These valves are the only ones contacting the reactive gas after it leaves the pretreater in its normal course of flow. Other valves in this sytem such as on the reactor by-pass line, gas control sample points, etc., are made of AISI Type 304 stainless steel.

All materials except those discussed above are of the conventional carbon steel or brass construction.

Design Calculations.--

(a) Velocity Computations: Many of the equipment design calculations were simple gas velocity computations. Important ones of this class were those involved in the CO pretreater, the reactor, the dust settler, and the fluidized solids temperature bath. For the pretreater, reactor, and dust settler, the computations were based on an experimental gas rate of one standard cubic foot per hour and atmospheric pressure operations. The design values of these velocities, as well as design temperatures and reasons for design values, are given in Table A-I.

(b) Energy Calculations: Other important design calculations were concerned with the heating systems, i.e., heating of the CO pretreater, and the fluizied solids temperature bath. In these calculations, sensible heat requirements for the reactants and heats of reactions were of minor significance. In the pretreater, significant heat loads included sensible heat requirements of the pretreater during the heat-up period and heat losses to the atmosphere. That is, heat-up time was the critical factor in sizing the heating elements for this system. A standard tubular resistance heater with a rated capacity of 1000 watts and a maximum allowable

Table A-I

Design Velocities

Location	Velocity	Temperature	Reason for Design Velocity
Pretreater	0.80 Ft./Sec.	700° F.	This velocity was determined by the dimensions of the tubing available. Confined to this tubing size, the velocity was then used to determine length of coil for about 15 seconds residence time.
Reactor	1.0 Ft./Sec.	1000° F.	This velocity was selected in order to allow reaction of powdered metals of size suitable for X-ray diffraction analysis (about 50 microns) with little solids entrainment by the reaction gas.
Dust Settler	0.002 Ft./Sec.	atmospheric	This velocity allows collection of graphite particles of the order of four microns and larger in diameter.
Fluidized Solids Bath	0.3 Ft./Sec.	1000° F.	This velocity considered suitable for fluidization of the solid material in the bath. This material is used type 3-A catalytic cracking catalyst.

sheath temperature of 1500° F. was specified. This allowed heating to 700° F. in about one hour with sufficient allowable thermal gradients for the required heat transfer rates. In the fluidized solids temperature bath, heat-up time was again the critical factor in sizing the heaters. Significant heat loads, in this case, included sensible heat requirements of the bath and the fluidization gas, as well as heat losses to the atmosphere. As usual, the calculations in this heating system were simplified for design purposes. That is, estimated quantities of materials and constant physical properties (such as specific heats, thermal conductivity coefficients, etc.) were assumed. The following basis was used for calculations.

A. Mass of steel in system to be heated --- 200 pounds.

B. Mass of fluidized solids to be heated --- 150 pounds.

C. Mass of insulation to be heated --- 100 pounds.

D. Flow rate of fluidization air --- 52 pounds/hour.

E. Specific heat of steel --- 0.12 BTU/pound-degree F.

F. Specific heat of fluidized solids --- 0.21 BTU/pound-degree F.

G. Specific heat of insulation --- 0.22 BTU/pound-degree F.

H. Specific heat of air --- 0.25 BTU/pound-degree F.

I. Insulation thickness --- 0.5 feet.

J. Thermal conductivity coefficient of insulation ---
0.14 BTU/hour-foot-degree F.

K. Equivalent heat loss transfer surface --- 30 square feet.

L. Outside surface temperature --- 100 degrees F.

M. Initial air, steel, insulation, and solids temperature ---
70 degrees F.

Using the above thirteen quantities, an approximate energy balance can be written on the temperature bath. This balance, in the usual form of "Input minus Output equals Accumulation," gives:

$$(1)\quad dQ/d\theta - (D)(H)(T - 70) - (J)(K)(T - 100)/(I) = \left[(A)(E) + (B)(F) + (C)(G)/2 \right] dT/d\theta$$

where, Q = heat input, BTU.

T = temperature, degrees F.

θ = time, hours,

and d denotes the differential operator.

For a constant heat input rate, Equation (1), when the above values are inserted and simplified, becomes,

$$(2)\qquad dT/(T - 81.8 - 159.2\ dQ^*/d\theta) = - 0.322\ d\theta$$

where $dQ^*/d\theta$ is the heat input rate (a constant) in kilowatts.

Integration of Equation (2) and substitution of initial conditions (i.e., $\theta = 0$, T = 70) yields,

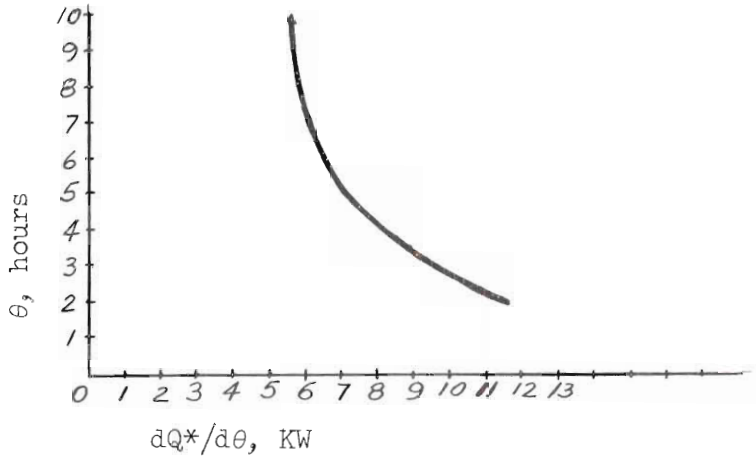
$$(3)\quad \ln\left[\frac{T - 81.8 - 159.2\ dQ^*/d\theta}{- 11.8 - 159.2\ dQ^*/d\theta}\right] = - 0.322\ \theta$$

where ln denotes natural logarithm.

Then for approximate times required to heat the system to 1000° F., as a function of heat input rate, Equation (3) can be simplified to,

$$(4)\quad \ln\left[\frac{5.77 - dQ^*/d\theta}{-0.074 - dQ^*/d\theta}\right] = - 0.322\ \theta$$

A graph of $dQ^*/d\theta$ versus θ from Equation (4) follows.



Based on these calculations and on standard equipment availability, three 2000 watts heating elements (operated on independent non-controlled circuits) and a 2250 watts circuit (operated on a controlled circuit) were selected for installation in the temperature bath. Heating times to bring the system up to 1000° F. actually were about 3.5 hours as compared to the value of about 3.75 hours calculated above. Equation (4) implies that steady state conditions at 1000° F. requires about 5.77 kilowatts heat input. Practice indicated that this was slightly over 6 kilowatts. The actual heating curves of temperature versus time, however, were not in as good agreement as these two comparisons over the entire range from 70 to 1000° F. (see Figure A-6).

Heating element temperatures were also estimated for the purpose of specifying necessary operating temperatures for required heat transfer rates. Experience has shown that a conservative estimate of heat transfer coefficients in fluidized beds is about 100 BTU/hour-square foot-degree F. Heat densities of the operating electrical heaters are about 10,000 BTU/hour-square foot. These calculations indicated the expected thermal

gradients, between heating elements and the fluidized bed, to be of the order of 100° F. Hence, elements with rated maximum operating sheath temperatures of 1500° F. were considered quite satisfactory for reactor operations up to 1100° F.

(c) Fluidization Gas Control Calculation: Compressed air was available at pressures up to 100 pounds/square inch gauge. This air was used as fluidization gas. The design used for controlling the flow rate of the fluidization gas was a restriction, or free-flow, orifice. The equation for sizing such an orifice may be found in Chemical Engineer's Handbook (32), page 403, equation (14). The orifice (sharp-edged) size was calculated on the basis of an upstream temperature of 70° F., upstream pressure of 100 pounds/square inch gauge, and a discharge coefficient of 0.8 to deliver 52 pounds per hour of air. This size was 3/32 inch diameter.

Calibrations and Engineering Data.--

(a) Calibrations of Rotameters: Calibrations were obtained for the gas rotameters and the fluidized solids temperature recorder controller. Engineering data were obtained for the experimental gas system loss rate (cold) and the fluidized solids temperature bath heat-up rate.

Figures A-1 and A-3 give the gas flow rate versus rotameter scale reading (with parameters of rotameter operating pressure) for the CO rotameter and the N_2 rotameter, respectively. Figures A-2 and A-4 give the gas flow rate versus rotameter operating pressure (with rotameter scale reading parameters) for the CO and N_2 rotameters, respectively. These calibrations were made using the service pressure gauges and a wet test meter at atmospheric temperature.

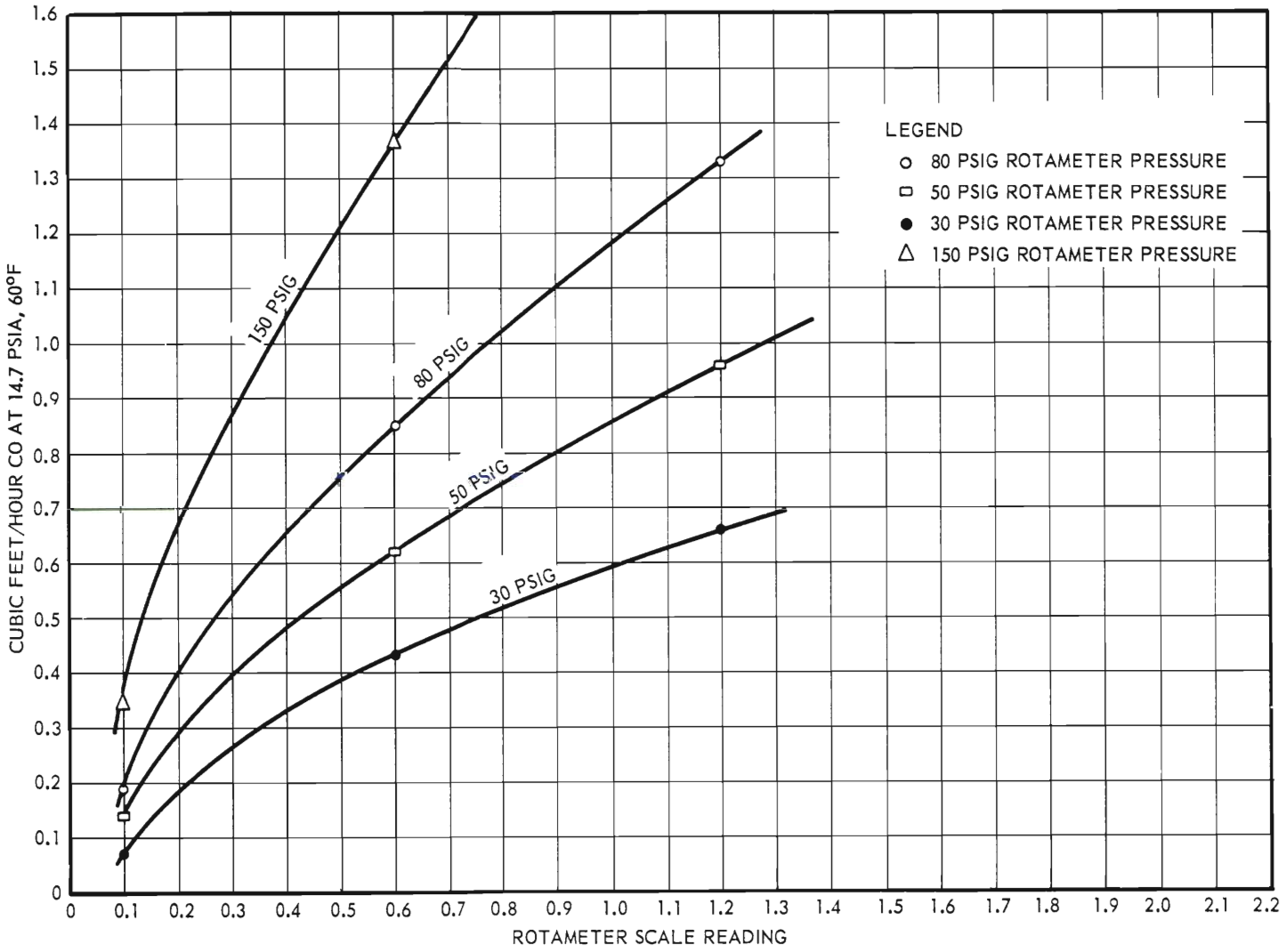


Figure A-1. CO Rotameter Calibration Curve.

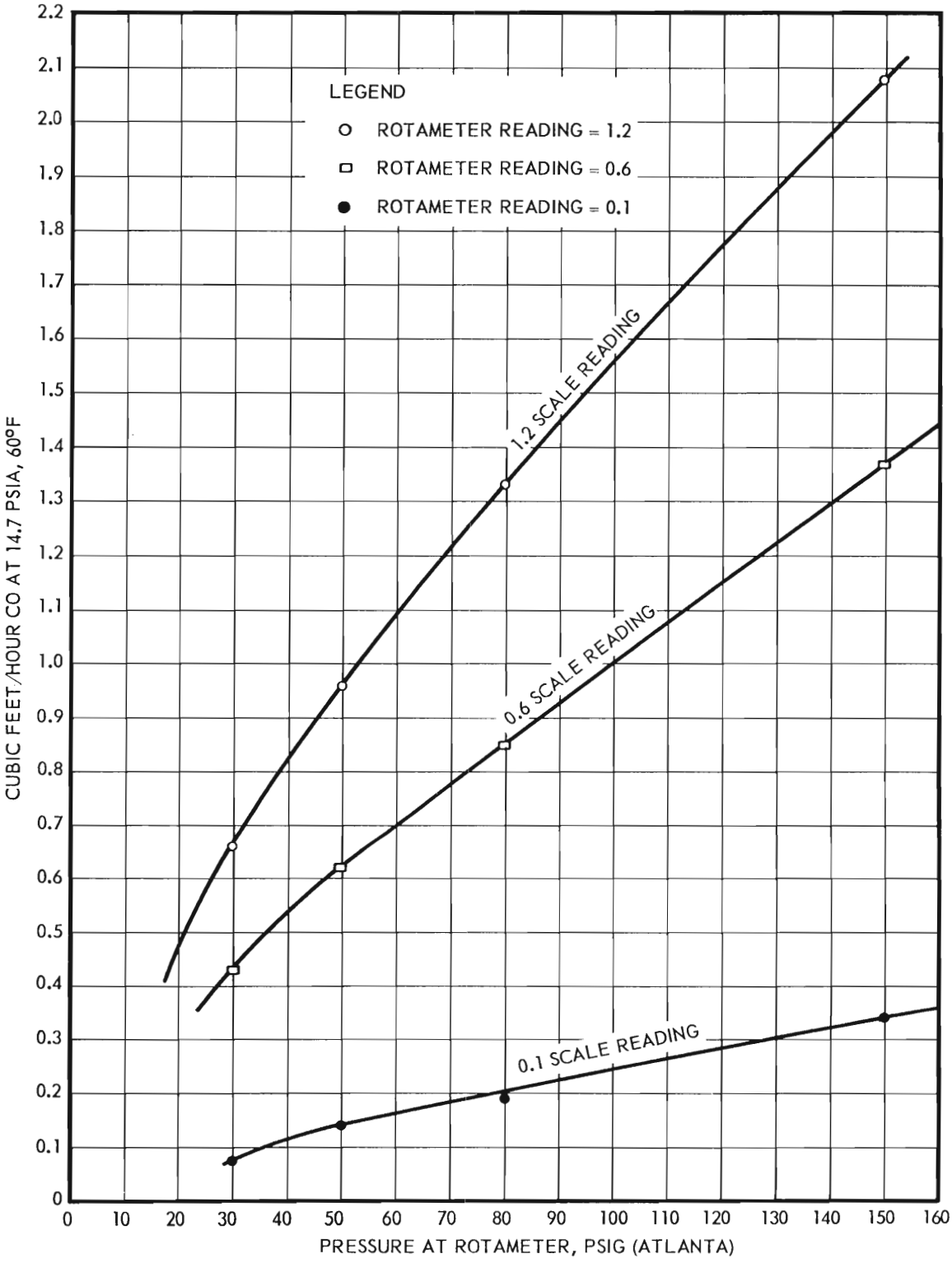


Figure A-2. CO Rotameter Calibration Curve.

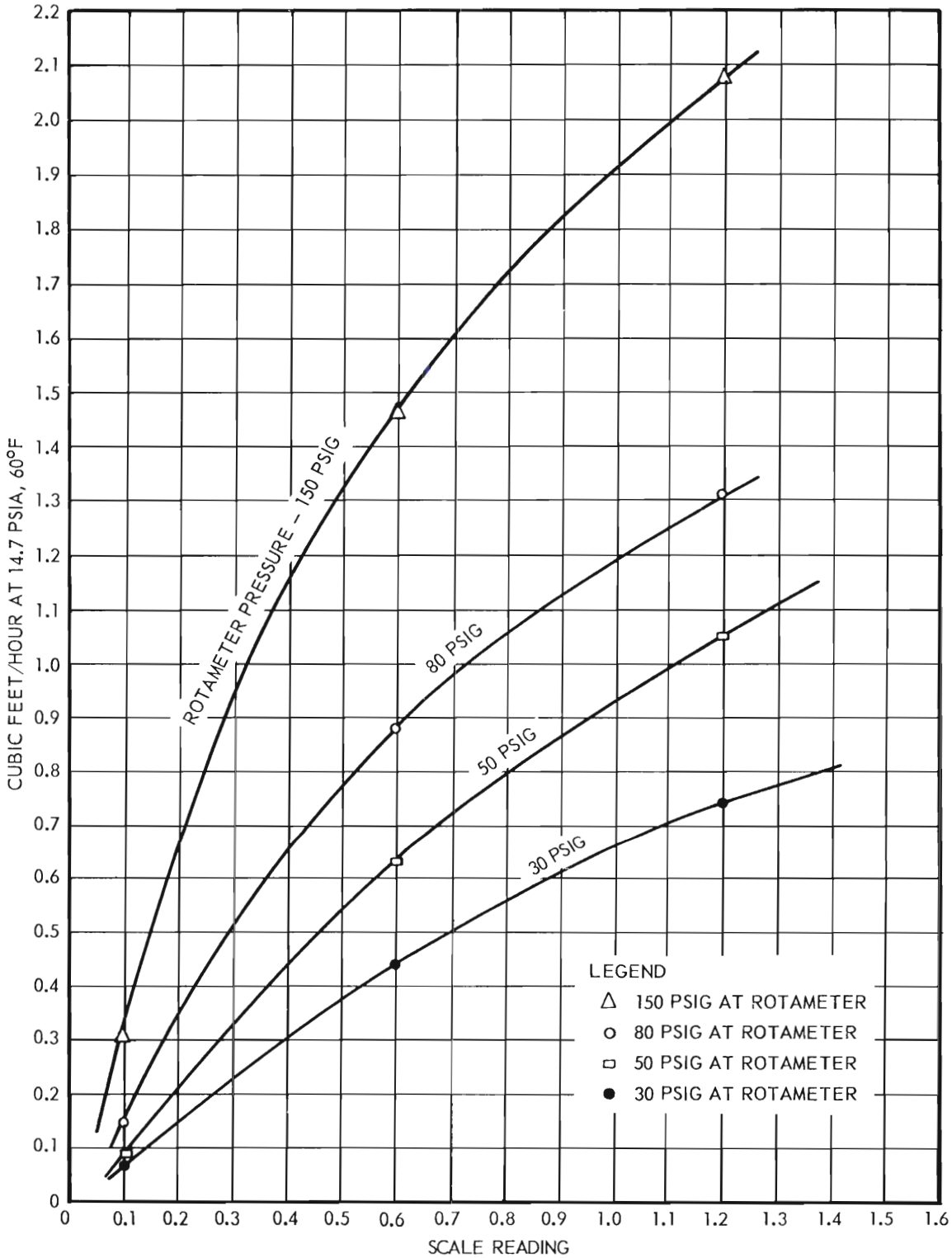


Figure A-3. N_2 Rotameter Calibration Curve.

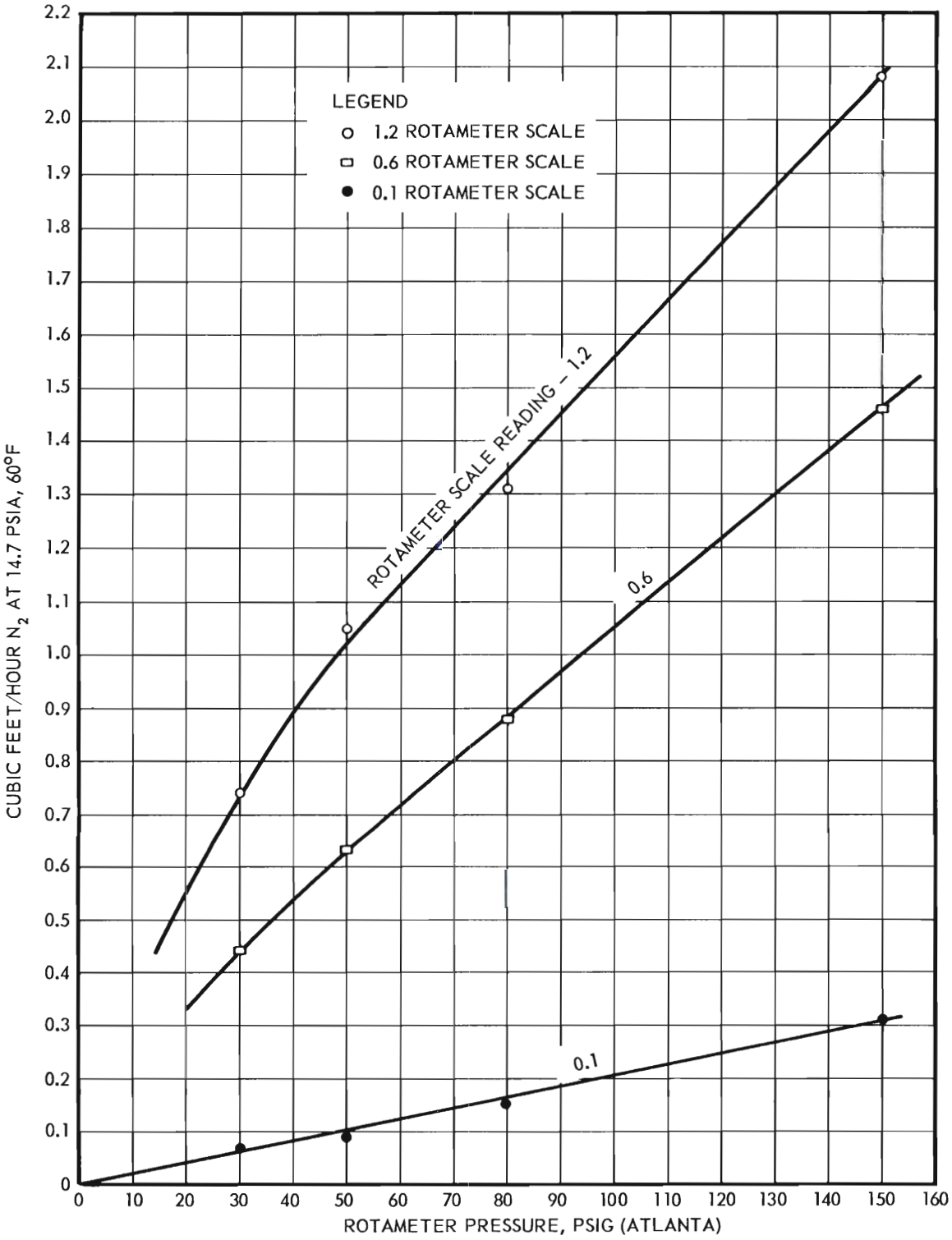


Figure A-4. N_2 Rotameter Calibration Curve.

(b) Calibrations and Checking of Temperature Control: A series of temperature measurements in the reactor were made using a calibrated chromel-alumel thermocouple and a potentiometer. This thermocouple had been previously calibrated against a platinum-platinum/rhodium (10%) thermocouple which was calibrated by the National Bureau of Standards. The Pt-Pt/Rh thermocouple had a rated accuracy of $\pm$ 1° C. As the temperatures were measured, using the above mentioned chromel-alumel thermocouple, simultaneous readings of the fluidized solids bath temperature recorder values were taken. For this set of test data, the temperature recorder values averaged 2.2° F. higher than those obtained with the calibrated thermocouple and potentiometer. There were 19 observations of temperatures at levels ranging from about 910 to 1000° F. The temperature recorder took its e.m.f. signal from the service chromel-alumel thermocouple located in the thermowell. This thermowell was in the operating location. The calibrated thermocouple measurements were made by inserting the bare couple into the reactor at various positions ranging in elevation from about 6 to 16 inches above the fluidized solids gas distributor plate. While these measurements were being made, nitrogen was passed through the reactor at the rate of one standard cubic foot per hour. There was variation in the temperature differences between the recorder and the calibrated thermocouple. That is, from the 19 observations, a standard deviation of $\pm$ 4.1° F. for the temperature differences was computed. Assuming a normal error distribution in this case, one concludes that the recorded temperature values average about 2.2° F. higher than the reactor temperature and an individual observation varies less than about $\pm$ 8.2° F. from this value for about 95% of the

observations. Temperature measurements in the reactor were also made at an elevation near the bottom of the fluidized bed (at the gas distributor plate). Nine observations were made at an elevation of about 3 inches above the fluidization gas distributor plate for the same temperature range and measuring procedure described above. The effect of the cold entering fluidization gas was indicated in this case. The recorded temperature value averaged 20.4° higher than the calibrated thermocouple value (the recorder thermocouple was in the same position as before, i.e., the operating position). A value of $\pm$ 7.1° F. was computed for the standard deviation of temperature variation from these 9 measurements. For the 19 measurements at the 6 to 16 inch elevation, the temperature differences were indicated to be rather random and were not indicated to be a function of elevation.

(c) Pressure Testing of Equipment: After the reaction gas system was constructed, a pressure test was made. For this test, the entire gas system (from the cylinder manifolds through the reaction product gas sample bomb) was pressured to 150 pounds/square inch gauge with dry nitrogen. The entire system was sealed off (by closing the operating valves) and then allowed to stand. System pressures were recorded as a function of time. These pressure decay data were used to estimate the gas loss rate versus system pressure relation given in Figure A-5. The entire system was at atmospheric temperature during this test.

Figure A-6 gives the results of a temperature bath heat-up time test. These data were taken from the fluidized solids temperature bath recorder-controller chart. All heaters (8.25 KW) were on and the rest of the system was in its operating state. For this particular set of experimental data,

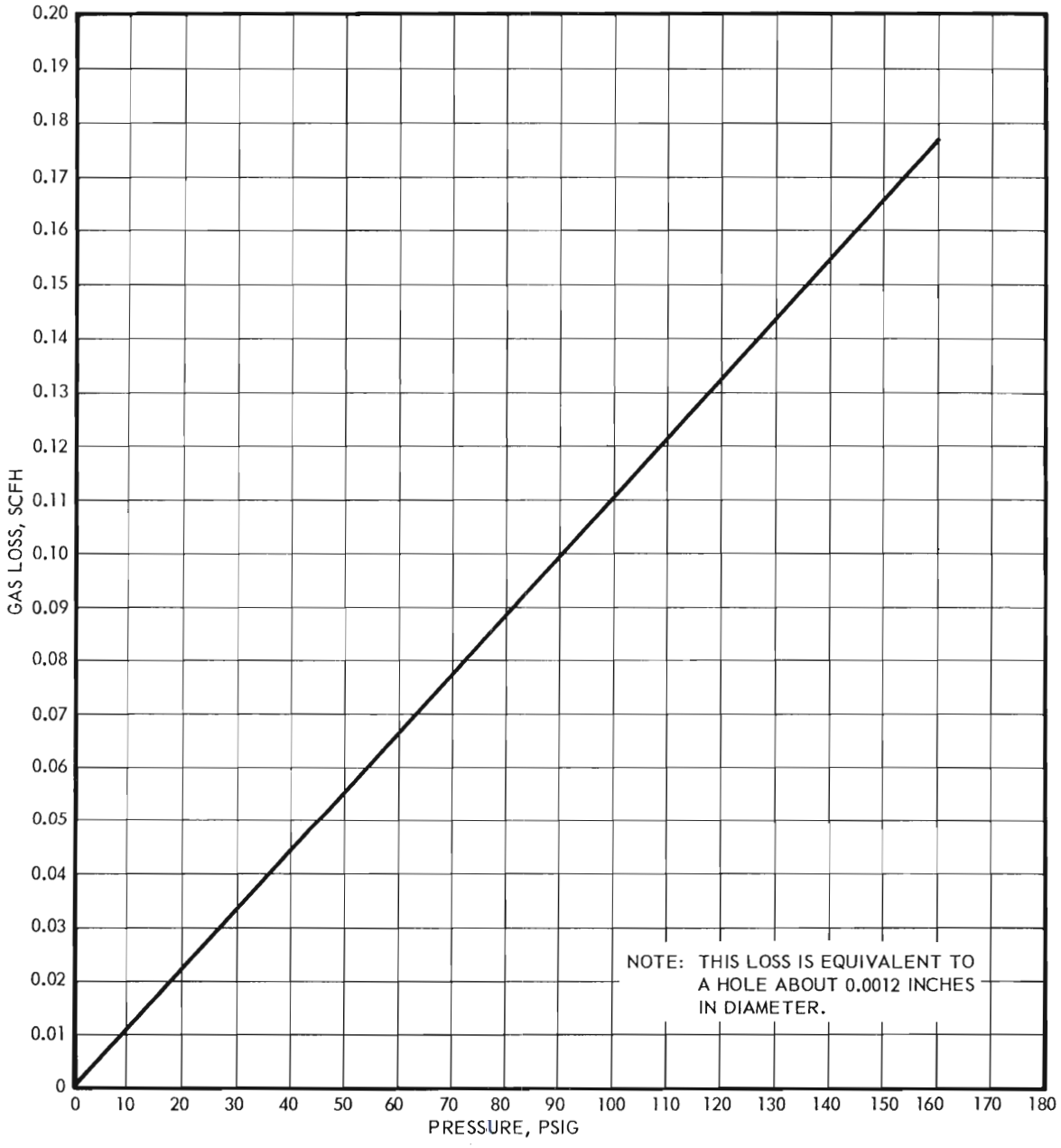


Figure A-5. Gas Loss in N_2 and CO Manifold and Rotameter System.

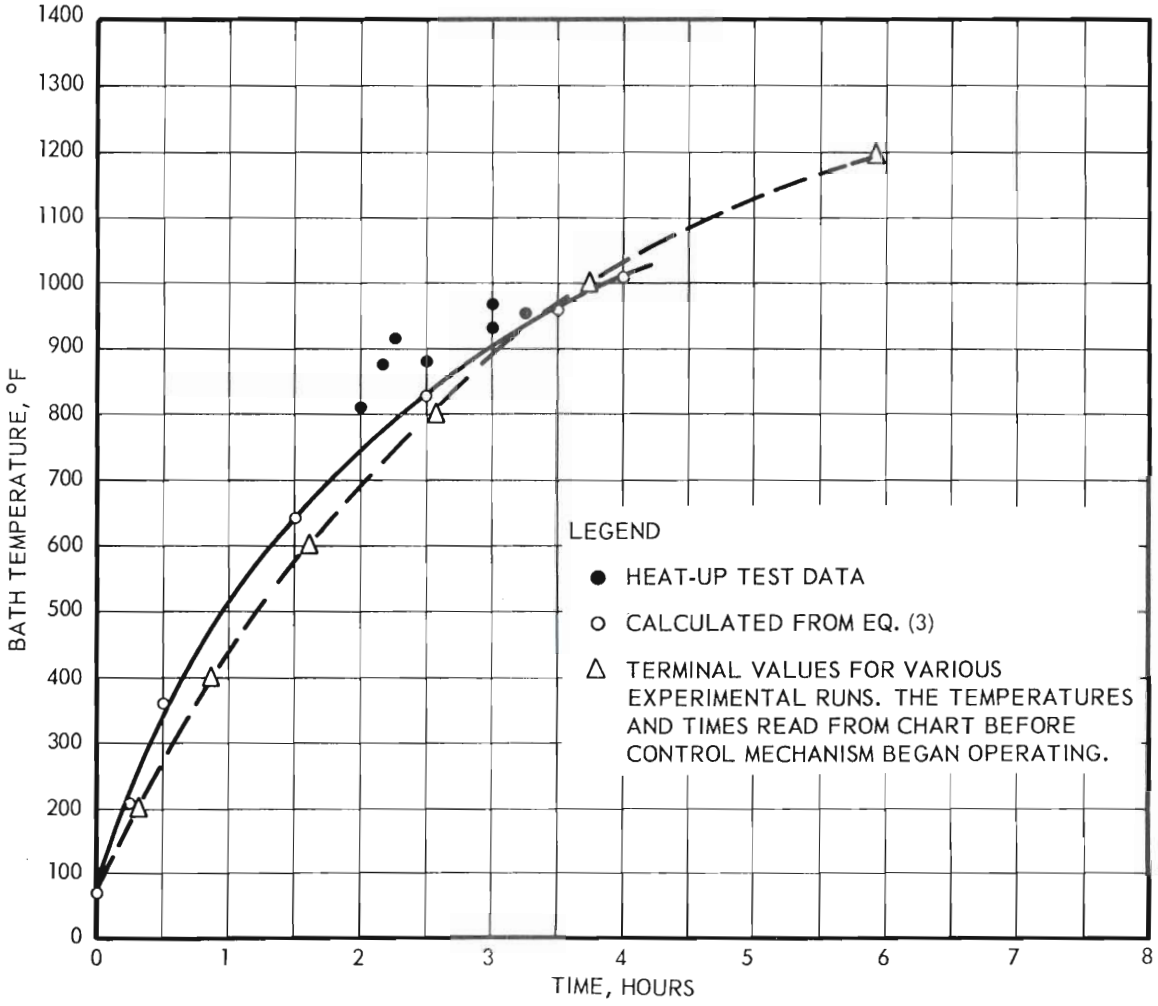


Figure A-6. Fluidized-Solids Temperature Bath Heating Times.

the heat-up time required for 1000° F. was about 3.9 hours. Also shown in Figure A-6 is a temperature-time curve calculated from equation (3). This curve fairly well agrees with the experimental test curve. In addition to these two curves, various spot points from seven operating runs are included on this graph. These point values were taken from the recorder chart just prior to the beginning of the control circuits (2.25 KW of the total 8.25 KW heat supply) activation. They tend to show that heat-up times are usually somewhat less than equation (3) indicates, at least for temperatures less than 1000° F.

Experimental Procedure.--The experimental procedure followed when subjecting metallic wire specimens to CO containing gases is outlined below. This does not include analytical work performed after the experimental exposure cycle was complete.

A. Sample and apparatus preparation.

1. Turn on temperature bath fluidization gas.
2. Turn on electric heaters in temperature bath and set temperature controller at desired reaction temperature.
3. Wind wire specimen (about 100 to 130 feet) on spindle to make bundle twelve inches long and about one-quarter inch diameter (loose strands).
4. Wash wire specimen twice with about 200 c.c. (each washing) hot (ca. 200° F.) toluene, allowing about 10 minutes washing time.
5. Dry wire specimen by moderate heating to about 300° F. and place in dessicator.

6. Weigh wire specimen on analytical balance (sensitivity - 10^{-4} gm.).
7. Fill CO gas purity cold trap with dry ice and acetone.
8. Turn on electric heater in CO pretreater and set temperature controller at desired pretreat temperature.
9. Flush nitrogen through CO pretreater and reactor for about 1 hour.
10. If reactor temperature is near desired reaction value, place metal specimen, from 6 above, in reactor.
11. Start CO flow through pretreat and cold trap (by-passing reactor) and allow to run for about one hour.
12. Check CO gas system for leaks.
13. Take pretreated CO sample and run Orsat analysis.
14. If CO analysis is satisfactory, inspect cold trap for condensed carbonyls - if no condensate, sample and apparatus preparation is complete.

B. Experimental Period.

1. Set reactor temperature, pretreat temperature, and reaction gas rate on desired values.
2. Start reaction gas through reactor.
3. Record reactor temperature, CO pretreater temperature, reactor pressure, fluidization gas pressure (high pressure side of orifice), reaction product gas vent pressures, rotameter pressures, rotameter scales readings, and reaction product gas analysis (Orsat) hourly.*

---

*At night, the experiment is allowed to run unattended. During this time, the only data recorded are by automatic temperature recorders.

4. When desired reaction time has been attained, turn heat off temperature bath, and start flushing gas system with dry nitrogen. (A reaction product gas sample may be taken in the bomb at this time if control Orsat analyses during run have indicated justification for this.)
5. When about 1 standard cubic foot of nitrogen (equivalent to about 3 times the gas system volume) has been flushed in, stop gas flow.
6. Open reactor, remove sample and place in dessicator.
7. Weigh cooled metal sample on analytical balance.

APPENDIX B

TABLE B–I

EXPERIMENTAL RESULTS ON EXPOSURES OF TYPE 304 STAINLESS STEEL WIRES TO CARBON MONOXIDE

EXPOSURE TIME: 16 HOURS. CARBON MONOXIDE RATE: 0.94 TO 1.03 (0.97 AVERAGE) CUBIC FEET (AT 14.7 p.s.i.a. AND 60°F.) PER HOUR

EXPERIMENT OR RUN NUMBER	WIRE SPECIMEN				EXPOSURE TEMPERATURE, °F.*	CO_2 CONTENT OF CO, VOLUME PER CENT**		REMARKS
	WEIGHT, GRAMS		WEIGHT INCREASE					
	INITIAL	FINAL	GRAMS	PER CENT		INITIAL	FINAL	
12	12.4442	12.4624	0.0182	0.15	1020[e]	<0.1	0.1 – 0.3	
13	12.1331	12.1453	0.0122	0.11	965[b]	<0.1	0.1 – 0.3	
14	12.6313	12.6481	0.0168	0.13	1065[c]	0.6	0.7 – 0.9	HIGH CO_2 CONTENT CARBON MONOXIDE.
15	12.2247	12.2490	0.0243	0.19	1065[b]	0.5	0.6 – 0.8	HIGH CO_2 CONTENT CARBON MONOXIDE.
16	12.6395	12.6478	0.0083	0.07	1020[b]	0.5	0.5 – 0.7	HIGH CO_2 CONTENT CARBON MONOXIDE.
17	12.3377	12.4314	0.0937	0.76	1060[b]	0.5	0.5 – 0.6	HIGH CO_2 CONTENT CARBON MONOXIDE.
18	12.3583	12.4256	0.0673	0.54	1055[a]	0.2	0.3 – 0.4	
19	12.6274	12.6401	0.0127	0.10	1015[b]	0.2	0.3 – 0.4	
20	12.4780	12.4815	0.0035	0.03	920[a]	0.2	0.2 – 0.4	
21	12.6176	12.6320	0.0144	0.11	965[c]	0.2	0.3	
29	12.6966	12.7651	0.0685	0.54	1070[e]	<0.1	0.4 – 0.5	
30	12.8045	12.9290	0.1245	0.97	1100[a]	0.2	0.4 – 0.6	

* Reactor temperature recorder-controller chart average to the nearest 5° F.

**Orsat determinations. These determinations must be treated as very qualitative at these levels of measurement. [a, b, c, d, e] Notation for indicating temperature variation during exposure period. Ranges of temperatures recorded on instrument chart (highest minus lowest, approximately): a, 5°F.; b, 10°F.; c, 15°F.; d, 20°F.; e, 30°F.

APPENDIX B

TABLE B-II

EXPERIMENTAL RESULTS ON EXPOSURES OF TYPE 304 STAINLESS STEEL WIRES TO CARBON MONOXIDE AT VARIOUS RATES AND TIMES

EXPERIMENT OR RUN NUMBER	WIRE SPECIMEN				EXPOSURE		CARBON MONOXIDE		RATE***	REMARKS
	WEIGHT, GRAMS		WEIGHT INCREASE		TEMPERATURE, °F.*	TIME, HOURS	CO_2 CONTENT**			
	INITIAL	FINAL	GRAMS	PER CENT			INITIAL	FINAL		
23	12.5021	12.5473	0.0452	0.37	1025[c]	16	0.2	0.4 – 0.6	0.27	
25	12.9899	13.1733	0.1834	1.41	1100[d]	16	0.2	0.4 – 0.8	0.29	
27	11.9939	12.1720	0.1781	1.49	1105[e]	16	0.3	0.4 – 0.6	0.29	WIRE SPECIMEN ACID TREATED****.
31	12.3602	12.4105	0.0503	0.41	1065[a]	16	0.2	0.4 – 0.6	0.26	
24	12.3082	12.5754	0.2672	2.13	1065[d]	32	0.2	0.2 – 0.4	0.94	
2a[1]	12.3932	12.5993	0.2061	1.67	1105[b]	32	--	0.3 – 0.5	0.93	
26	12.4678	12.7315	0.2637	2.11	1065[e]	120		0.1 – 0.6	0.92	2 CYLINDERS CO USED, 0.1, 0.2% CO_2.
22	12.2999	12.3501	0.0502	0.41	1100 – 965	16	0.2	0.4 – 0.8	0.3 – 1.0	EQUIPMENT FAILURE, RUN RUINED.
28	12.3570	12.6095	0.2545	2.05	1130 – 1020	ca. 46	<0.1	0.1 – 0.7	0.30	EQUIPMENT FAILURE. ABOUT 26 HOURS EXPOSURE NEAR 1100°F. AND ABOUT 20 HOURS EXPOSURE BETWEEN 1020 AND 1080°F.

* Reactor temperature recorder-controller chart averages to nearest 5°F.

** Orsat determinations in volume per cent. These determinations must be .reated very qualitatively at these levels of measurement.

*** Carbon monoxide rates in cubic feet (measured at 14.7 p.s.i.a. and 60°F.) per hour.

****Run 27 wire specimen was boiled in concentrated nitric acid for 16 hours resulting in a weight decrease of about 0.51 per cent. This acid treatment was done on the "as received" wire before exposure to carbon monoxide in Run 27.

[1] All experimental run numbers increase chronologically, regardless of metal specimen type, exposure conditions, etc. However, Runs 1a, 2a and 3a began a new series which followed all experiments numbered 2 through 31 in Tables B-I, B-II and D-I.

a, b, c, d, e Notation for indicating temperature variations during exposure periods. See footnote in Table B-I for details.

APPENDIX C

Results of X-ray Diffraction Analyses of Experimental Wires and Carbonaceous Surface Deposits.

Analysis Number 1. Run Number --. X-ray Specimen: Nickel wire. Radiation: Copper (40 Kv, 20 ma). Filter: Nickel. X-ray Exposure Time: 3 hours. Type Analysis: Powder Camera.

d:	2.02	1.76	1.24	1.06	1.02	0.88	0.81	0.79
I:	VS	S	M	S	W	W	M	M

Suggested identifiable crystalline structure: face-centered cubic, a = 3.52

Possible experimental diffraction lines not reported: None.

Analysis Number 2. Run Number 2. Specimen: CO exposed Ni wire. Radiation: Copper (40 KV, 20 ma). Filter: Nickel. X-ray Exposure Time: 6 hours. Type Analysis: Powder Camera.

d:	2.02	1.76	1.24	1.06	1.02	0.88	0.81	0.79
I:	VS	S	M	S	W	W	M	M

Suggested identifiable crystalline structure: face centered cubic, a = 3.52

Possible experimental diffraction lines not reported: None.

Results of X-ray Diffraction Analyses of Experimental Wires and Carbonaceous Surface Deposits. (Continued)

Analysis Number 3. Run Number --. X-ray Specimen: Inconel wire. Radiation: Copper (40 KV, 20 ma). Filter: Nickel. X-ray Exposure Time: 12 hours. Type Analysis: Powder Camera.

d:	2.05	1.78	1.26	1.07	1.03	0.89	0.82	0.80
I:	VS	M	S	S	W	W	M	M

Suggested identifiable crystalline structure: face centered cubic, a = 3.56

Possible experimental diffraction lines not reported: None.

Analysis Number 4. Run Number 1a. X-ray Specimen: Exposed Inconel wire. Radiation: Molybdenum (45 KV, 20 ma). Filter: Zirconium. X-ray Exposure Time: 12 hours. Type Analysis: Powder Camera.

d:	2.04	1.76	1.24	1.07	1.02	0.88	0.81	0.79	0.72	0.68
I:	VS	S	S	S	M	W	M	M	W	W

Suggested identifiable crystalline structure: face-centered cubic, a = 3.53

Possible experimental diffraction lines not reported: 11.

Analysis Number 5. Run Number --. Specimen: Type 304 steel. Radiation: Molybdenum (45 KV, 20 ma). Filter: Zirconium. X-ray Exposure Time: 12 hours. Type Analysis: Powder Camera.

d:	2.06	1.79	1.27	1.08	1.04	0.89	0.82	0.81	0.73	0.61
I:	VS	S	S	S	M	W	M	W	W	W

Suggested identifiable crystalline structure: face centered cubic, a = 3.58

Possible experimental diffraction lines not reported: 14.

Results of X-ray Diffraction Analyses of Experimental Wires and Carbonaceous Surface Deposits. (Continued)

Analysis Number 6. Run Number --. Specimen: Type 304 steel. Radiation: Copper (40 KV, 20 ma). Filter: Nickel. Type Analysis: Diffractometer. Scan: $2\theta = 160°$, 1/2°/minute.

d:	2.08	1.80	1.43	1.27	1.09	0.93
I/I_o:	100	40	16	37	19	12

Suggested identifiable crystalline structure: face centered cubic, a = 3.63

Possible experimental peaks not reported: 10.

Analysis Number 7. Run Number 12. Specimen: CO exposed Type 304 steel wire. Radiation: Copper (40 KV, 20 ma). Filter: Nickel. Type Analysis: Diffractometer. Scan: $2\theta = 160°$, 1/2°/minute.

d:	2.08	1.81	1.44	1.28	1.09	0.94
I/I_o:	100	44	11	36	13	13

Suggested identifiable crystalline structure: face centered cubic, a = 3.64

Possible experimental peaks not reported: 8.

Analysis Number 8. Run Number 25. Specimen: Cleaned wire from Run 25. Radiation: Chromium (50 KV, 10 ma). Filter: Vanadic oxide. X-ray Exposure Time: 12 hours. Type Analysis: Powder Camera.

d:	2.08	1.81	1.28
I:	VS	M	S

Suggested identifiable structure: face centered cubic, a = 3.61

Number of possible experimental lines not reported: 6.

Results of X-ray Diffraction Analyses of Experimental Wires and Carbonaceous Surface Deposits. (Continued)

Analysis Number 9. Run Number 25. Specimen: Surface deposit. Radiation: Molybdenum (45 KV, 20 ma). Filter: Zirconium. X-ray Analysis Type: Diffractometer. Scan: $2\theta = 60°$, 1/2°/minute.

d:	3.37	2.95	2.66	2.06	2.04	2.03	2.02	1.78	1.44	1.16
I/I_o:	72	12	10		75		100	28	10	10

Suggested identifiable structure: graphite, face centered cubic, a = 3.56, body centered cubic, a = 2.85. Possible peaks not reported: 11.

Analysis Number 10. Run Number 24/26. Specimen: Surface deposit. Radiation: Molybdenum (45 KV, 20 ma). Filter: Zirconium. Type Analysis: Powder Camera. X-ray Exposure Time: 12 hours.

d:	3.39	2.05	1.79	1.26	1.17	1.08
I:	VS	VS	S	W	M	W

Suggested identifiable structure: graphite and face centered cubic, a = 3.57

Possible experimental diffraction lines not reported: 14.

Results of X-ray Diffraction Analyses of Experimental Wires and Carbonaceous Surface Deposits. (Continued)

Analysis Number 11. Specimen: Carbonaceous deposit from an industrial corrosion specimen*. Radiation: Molybdenum (45 KV, 20 ma), X-ray Exposure Time: 6 hours. Filter: Zirconium. Type Analysis: Powder Camera.

d:	3.37	2.03	1.77	1.67	1.25	1.17	1.07
I:	VS	VS	S	M	M	W	W

Suggested identifiable structure: graphite and face centered cubic, a = 3.54

Possible experimental diffraction lines not reported: 2.

d = lattice spacing, Å. I = intensity. I/I_o = relative intensity. M = medium. S = strong. V = very. W = weak.

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*The specimen in Analysis 11 was taken from a pit in a piece of Inconel which had been in industrial service. This Inconel specimen is described on page 74.

APPENDIX D

TABLE D–1

EXPERIMENTAL RESULTS ON EXPOSURES OF INCONEL AND COMMERCIALLY PURE NICKEL TO CARBON MONOXIDE, FOR VARIOUS TIMES

WIRE DIAMETERS: INCONEL – 0.008 INCH, NICKEL – 0.01 INCH. CO RATE: 0.92 – 0.99 (0.96 AVERAGE) CUBIC FEET[1] PER HOUR.

EXPERIMENT OR RUN NUMBER	MATERIAL	WIRE SPECIMEN				EXPOSURE		CO_2 CONTENT OF CO, VOLUME PER CENT**		REMARKS: NONE.
		WEIGHT, GRAMS		WEIGHT INCREASE		TEMPERATURE, °F.*	TIME, HOURS	INITIAL	FINAL	
		INITIAL	FINAL	GRAMS	PER CENT					
2	NICKEL	13.7052	13.7140	0.0088	0.064	960[b]	4	<0.1	0.4 – 0.6	
4	NICKEL	13.7898	13.7906	0.0008	0.006	1015[c]	4	<0.1	0.2 – 0.3	
5	NICKEL	14.0019	14.0025	0.0006	0.004	1015[c]	4	<0.1	0.2	
3	NICKEL	13.2620	13.2688	0.0068	0.051	1065[b]	8	<0.1	0.4 – 0.5	
3a[2]	NICKEL	13.1543	13.1588	0.0045	0.034	1105[c]	16	0.4	0.4 – 0.5	
6	INCONEL	11.2464	11.2470	0.0006	0.053	1015[c]	4	<0.1	0.2 – 0.3	
7	INCONEL	11.4122	11.4169	0.0047	0.041	1065[b]	16	<0.1	0.1 – 0.4	
8	INCONEL	12.0871	12.0926	0.0055	0.046	970[d]	16	<0.1	0.0 – 0.2	
9	INCONEL	11.3991	11.4077	0.0086	0.075	1020[c]	16	<0.1	0.1 – 0.3	
10	INCONEL	10.8802	10.8883	0.0081	0.074	945[c]	16	<0.1	0.0 – 0.1	
11	INCONEL	11.0134	11.0199	0.0065	0.059	945[a]	16	<0.1	0.0 – 0.1	
1a[2]	INCONEL	10.1590	10.1688	0.0098	0.097	1100[a]	16	0.4	0.6	

* Reactor temperature recorder-controller chart average to nearest 5° F.

**Orsat determinations. The determinations must be treated very qualitatively at these levels of measurement.

[1] Gas volumes measured at 14.7 p.s.i.a. and 60° F.

[2] Runs 1a and 3a made after the series numbered 1 through 31. Otherwise, run numbers are in chronological order.

APPENDIX E

TYPICAL COMPOSITIONS AND HISTORIES OF WIRES USED FOR EXPERIMENTATION

Compositions

Typical compositions of the experimentally studied metals are given in the following tabulation.

Typical Chemical Compositions, weight per cent.

Material	Fe	Cr	Ni	C	Mn	Si	S	Cu
Inconel	9.0 max.	12-15	75 min.	0.15 max.	1.0 max.	0.5 max.	0.02 max.	0.5 max.
Nickel	0.15-0.30		99.45	0.1-0.2	0.2-0.35	0.05-0.2	0.005-0.008	0.1-0.2
Type 304 Steel	Balance	18-20	8-11	0.06 max.	2.0 max.	1.0 max.		

History

The Wilbur B. Driver Company stated that the Inconel and nickel wires were drawn from 1/4 inch diameter hot rolled rod which had been annealed and pickled. Drawing was done with about 75 per cent reduction in area per draft. Lubricants used in the drawing operations were grease, oil, or soap. Intermediate annealing was done in strand annealing furnaces. Final annealing of the wires was done in an atmosphere of dissociated ammonia. The annealing temperatures were 1750° F. for nickel and 2150° F. for Inconel.

The Type 304 stainless steel wires were drawn from hot rolled rod of 5/16 inch or 1/4 inch diameter. These rods had been annealed and pickled. The drawing was done in stages which resulted in about 75 per cent reduction of area per draft. Intermediate annealing was done in strand annealing furnaces. The final annealing was at 2150° F. in an atmosphere of dissociated ammonia. The stainless steel wires were bare drawn in diamond dies when the diameters were less than 0.025 inch. For diameters greater than 0.025 inch, the stainless steel was hot dipped in lead for lubrication.

All wires used in the experimental work were taken from single wire spools of each of the three materials studied. These wires were donated by the Wilbur B. Driver Company, Newark, New Jersey. This company identified the material by melt numbers. For the three spools of experimental wires, the melt numbers were:

Inconel ..... Melt 436

Nickel ..... Melt 2706

Type 304 Stainless Steel ..... Melt 11987.

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